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KINETIC MECHANISMS GOVERNING THE FATE OF CHEMICALLY BOUND SULFUR AND NITROGEN IN COMBUSTION

C. V. Sternling, et al

Shell Development Company

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16. ABSTRACT

The report gives the results of an investigation of kinetic mechanisms governing the fate of chemically bound nitrogen and sulfur in combustion. A literature review led to several critical questions which were investigated using detailed computer simulations of reaction schemes considered to be relevant. The problem areas examined included the role of pyrolysis, mathematical modeling of a turbulent diffusion flame, kinetic mechanisms of NO formation and NO reduction, and kinetic mechanisms of the oxidation of SO2 to SO3. The report tentatively answers some of these questions, either from the literature survey or from the results of the computer simulations. The insights gained may lead to control of air pollutant emissions by combustion modifications.

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Sulfur	Cyanides	Quenching	EXHAUS	20M
Nitrogen	Pyrolysis	(Cooling)	CODEN	21B
Combustion	Catalysis		CHEMEQ	
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by

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144

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CONTENTS

Page

Purpose and Scope 1

Conclusions 2

Overall View of Combustion 3

Method of Documenting Arrhenius Constants for Reactions 7

Equilibrium Considerations 8

Literature Review 13

- Experimental Data on Fuel Nitrogen Conversion in Oil and Coal 13
- Combustion of Ammonia 17
- Cyanides and Combustion Using Nitrogen Oxides as the Oxidizer 20
- Oxidation of HCN 20
- Low-Temperature Mechanisms Involving N-N Bond Formation 21
- Pyrolysis 23
- Reactions Involving Sulfur 26
- Process Modifications to Reduce SO_3 Emissions 41
  - Low Excess Air Combustion 41
  - Flame Quench 42
  - Staged Combustion 42
    - Two-Stage Air Addition 42
    - Two-Stage Fuel Addition or Reburning 42
  - The Use of Additives 43
- Summary of Literature Review 44

Results of Modeling Studies 46

- "Prompt" NO by Cyanide Reactions 46
- Fixation of Atmospheric Nitrogen 48
- NO_x Reduction by Secondary Fuel Injection or Reburning 54

CONTENTS (CONT)

Page

Oxidation of Fuel Nitrogen in a Diffusion Flame 64

SO_2 Oxidation to SO_3 in Flames 72

Results Obtained From Merryman and Levy Kinetics 72

Results With Adjusted Rate Coefficients 77

Conclusions 77

Synergism Between Sulfur and Nitrogen Oxides (Post-Flame Region) 79

Recommendations for Future Work 82

Nomenclature 83

Appendix I. Library of Reaction Rate Data 85

Appendix II. Literature References Using the CODEN System 99

Appendix III. Simulation of Flame Fronts by "Point-Wise" Kinetic Calculations 125

Premixed Flat Laminar Flames 125

Diffusion Flames Modeled by the Whitman Two-Film Theory 128

Appendix IV. Description of Computer Program EXHAUS for Integrating Stiff Differential Equations Arising in Kinetics Problems 131

Abstract 131

Purpose and Scope 131

Output Generated 132

Sample Problem 132

Problem Setup 132

Appendix V. An Exhibit of the Computer Output Generated by Program EXHAUS 137

FIGURES

No.	Title	Page
1	Three Regimes of Particle or Droplet Combustion	4
2	Tentative Diagram Showing Paths Taken by Fuel Nitrogen in Coal Combustion	5
3	Tentative Diagram Showing Paths Taken by Fuel Nitrogen in Residual Oil Combustion	6
4	Equilibrium HCN in Combustion Gases	12
5	NO_x Concentration as a Function of Excess Combustion Air	16
6	Effect of Cracking Severity on Product Distribution in Gas-Oil Cracking	25
7	Equilibria of Sulfur Species in a 10% Excess Air Flue Gas	27
8	Equilibrium Levels of Plume Forming Species	28
9	The Variation of the Theoretical Equilibrium Yield and Possible Actual Yield of SO_3 with Time in a Boiler	30
10	Effect of Fuel Sulfur Level on SO_3 Formation	32
11	Effect of Fuel Sulfur Level on SO_3 Formation	33
12	Effect of Excess Air on SO_3 Formation	34
13	Effect of Excess Air on SO_3 Formation	35
14	Flame Formation of SO_3 as Function of Excess Air and Sulfur Level of Fuel	36
15	Typical Temperature Profile - Injector Not in Position	38
16	Effect of Flame Temperature on SO_3 Formation	40
17	Splitting of N-N Bonds, Lange Run 1	51
18	Production of N-O Bonds, Lange Run 1	52
19	Predicted and Experimental Temperatures for Computer Run NFIX4	57

FIGURES (CONT)

No.	Title	Page
20	Predicted and Measured NO_x Production	58
21	Mechanistic Models of Flame Sheets Occurring in Diffusion Flames	65
22	Flame Sheet Model for Situation B	66
23	Effect of Temperature on NO Production in H_2 Diffusion Flame	70
24	Effect of Temperature Quench on SO_3 Profiles - Merryman and Levy Kinetics	75
25	Attempts to Fit Merryman and Levy Mechanism and Rate Coefficients to Data of Cullis, Henson, and Trimm	76
AIII-1	Conceptual Sketch of Flame Front in a Laminar Premixed Flame	126
AIII-2	Conceptual Sketch for Diffusion Flame Front	129

TABLES

No.	Title	Page
1	Equilibrium Composition at 1200°K	8
2	Equilibrium for Reaction $HCN + 3/2\ CO_2 \longrightarrow 1/2\ N_2 + 1/2\ H_2O + 5/2\ CO$	10
3	Equilibrium for Six-Component System Calculated by CHEMEQ-90% of Theoretical Air Simulated No. 2 Fuel Oil	10
4	Equilibrium for 16-Component System Calculated by CHEMEQ-90% of Theoretical Air-Simulated No. 2 Fuel Oil	11
5	Mechanisms of NH_3 Oxidation	19
6	Nitrogen Compounds which Might be Involved in Linkage Reactions	23
7	Experimental Data on SO_3 Formation	37
8	Available Data on the Kinetic Constant of the Reaction $SO_2 + O + M \longrightarrow SO_3 + M$	44
9	Reactions Included in the Cyanide Route to Prompt NO	47
10	Arrhenius Parameters Used in Study of Prompt NO via Cyanides	47
11	Fixation of Atmospheric Nitrogen--Synopsis of Computer Runs	50
11a	Reactions Used for Combined Methane-Burning and Nitrogen Fixation	55
12	"Debris" from the Combustion of Methane with Air in a Premixed Flame	56
13	Reactions Used in Reburning Model	60
14	"NO" Reduction by Hydrogen. No "CO_2" in Mixture	61
15	NO Reduction in Presence of CO_2	63

TABLES (CONT)

No.		Page
16	Reactions Used in Hydrogen Diffusion Flame	69
17	Calculated Results-Hydrogen Diffusion Flames with Fuel Nitrogen Simulated by N Atoms	71
18	Basic Kinetic Scheme for SO_2 Oxidation	73
19	Results Using Adjusted Rates	78
20	NO-SO_2 Synergism	80
21	Application of Model for NO/SO_2 Synergism to Furnace Flue Gas and Sulfur Plant Incinerator Emissions	81
AI-1	Listing of IBM Cards for Reaction Rate Library	86
AI-2	Format for Reaction Rate Library	95
AI-3	Reaction Names--Conventions Used and Literature References	97
AII-1	List of References in Order of Acquisition Number	100
AII-2	Literature References Alphabetized by Author	106
AII-3	Literature References Alphabetized by CODEN	112
AII-4	CODEN Names for Journals, Alph by Name of Journ	118
AII-5	CODEN Names for Journals, Alpha by CODEN	120
AII-6	Complete References to Non-Periodical Literature	122
AIV-1	Format of Control and Data Cards	134
AIV-2	Format of Data Cards	136

Purpose and Scope

The objective of this work has been to elucidate the mechanisms by which nitrogen and sulfur which are chemically bound in the fuel molecules are converted into objectionable pollutants. This was attempted through detailed computer simulations of reaction schemes considered to be relevant. It was expected that the insights gained into the mechanisms of conversion would lead to ideas for the control of these pollutants by combustion modification and would help in interpreting the results of experimental studies. The work was requested by the U. S. Environmental Protection Agency as Task 14 of Contract EHS-D-71-45.

A review of the literature on the fate of fuel nitrogen and sulfur led to the formulation of the following critical questions:

1. To what extent does pyrolysis of the fuel occur before combustion?

2. How is the nitrogen bound in the pyrolysis products?

3. How is the nitrogen distributed among the pyrolysis products?

4. What is the environment (temperature and air-to-fuel ratio) at the flame front in a diffusion flame of finite thickness, and how does this environment affect the yield of products from the fuel nitrogen?

5. What reactions contribute significantly to the fixation of atmospheric nitrogen both in the flame front and in the post-flame zone?

6. What are the reactions governing the rate of conversion of SO_2 to SO_3, both in the flame and in the post-flame region?

7. After NO has been formed, what reactions can reduce it back to N_2 and under what conditions are they effective?

Tentative answers are advanced for some of these questions, either from the literature survey or from the results of computer simulations. For the latter, the main tool used is the computer program EXHAUS which is described briefly in Appendix IV. EXHAUS is a general purpose program for the integration of the material and heat balance equations for either "point-wise" conditions or for a plug flow reactor. "Point-wise" calculations can be shown to include the perfectly stirred reactor and approximate simulations of flame fronts in either premixed or diffusion flames. Tentative reaction mechanisms were set up for six situations thought to be important for fuel nitrogen and sulfur conversion and were integrated using these programs. Valuable insights have been obtained from each simulation. Obviously, many approximations are required in work of this type; hence, each of the simulations can be elaborated. In most cases, however, the important features of the mechanisms can be seen from the current simplified simulations.

Problems simulated were:

1. Fixation of atmospheric nitrogen in premixed methane flames.

2. Formations of "prompt NO" via a reaction scheme involving cyanide intermediates.

3. Combustion of fuel nitrogen in a gaseous diffusion flame under various degrees of combustion intensity.

4. Reduction of NO back to N_2 by means of flame reactions.

5. Conversion of sulfur to SO_3 in flames.

6. Catalysis of SO_2 oxidation by oxides of nitrogen.

Conclusions

From this study, we reached the following conclusions:

1. A large fraction of the nitrogen in the fuel appears in the char fractions formed by pyrolysis, especially when the fuel is coal but also for residual oil fuels.

2. Among the gaseous products of pyrolysis, HCN is expected to be the most important.

3. The rate of fixation of atmospheric nitrogen cannot be predicted with confidence for all situations. More good data is required.

4. While the Zeldovich reactions (see reactions 19 and 20 in text) usually account for the bulk of the nitrogen fixed in flames, other reactions are sometimes important.

5. Two alternative explanations for the "prompt NO" reported by Fenimore can be advanced--fixation via cyanide intermediates or by reaction with the excess free radicals produced in the flame front. More data is required especially for fuels other than methane.

6. Fairly good quantitative predictions of prompt NO can be made by considering the interaction of the combustion reactions with the fixation reactions without cyanide intermediates.

7. The trends in the ratio of NO to N_2 produced by the combustion of molecules containing nitrogen as nitrogen content and temperature change can be predicted by a simple model of the diffusion flame front. The reverse of the Zeldovich fixation mechanism accounts for the production of N_2. A strong effect of combustion intensity is also predicted by this model.

8. An accurate quantitative description of the catalysis of the post-flame oxidation of SO_3 to SO_3 by the oxides of nitrogen has been developed. More data is required before the flame oxidation can be correctly modeled.

9. Reduction of NO by homogeneous gas reactions is possible in fuel-rich environments. The reaction with H_2 can be modeled using some of the reactions from the schemes of Lange and of Wilde. It was shown that the key reaction is

$$N + NO = N_2 + O \qquad (1)$$

and that the N atoms are produced from intermediate compounds such as HNO, NH, etc. Carbon dioxide inhibits the reduction according to this mechanism since it competes for the reducing agent, H_2, forming considerable CO.

Overall View of Combustion

Only the heavy, dirty fuels contain appreciable amounts of chemically bound nitrogen and sulfur. Useful models for predicting the conversion products resulting from combustion must be therefore applicable to such fuels (coal and the residual fuel oils). Because of their low volatility, these fuels cannot be premixed with the combustion air to form a gaseous mixture; hence, diffusion flames are universally used for their combustion. The physical processes governing combustion in diffusion flames of particulate matter are extremely complex and are still the subject of a large research effort. Modeling of the chemical mechanism of the combustion depends very strongly on the physical processes and, hence, cannot be very precise at this time. One needs to abstract the salient features of the combustion and make drastic simplifications in order to do practical chemical modeling.

Our view of droplet combustion is in terms of three regimes, which are illustrated schematically in Figure 1. The first regime occurs during periods of rapid volatilization and large relative velocities between the drop and the surrounding gases. Combustion occurs in the wakes trailing the particles; and the fuel and the oxidizer are premixed, though imperfectly, before combustion starts. The burning is then accomplished largely by (probably turbulent) flame fronts which sweep through the gas. The second regime, shown in Figure 1, occurs where the rate of vaporization is slow enough to allow a flame to attach itself to the particle. Here most of the combustion occurs in a thin flame sheet surrounding the particle and its wake. The reactions occurring in this diffusion flame sheet are quite different from those occurring in the premixed case. In particular, there are hot, fuel-rich regions where precombustion pyrolysis can occur. In such a flame front the "fuel" is therefore not the same as the material fed into the furnace. The third regime occurs after the more volatile materials have been vaporized. Because of the strong heating, the remnant of the particles containing the heavy ends is pyrolyzed very strongly and is thereby converted into a char. As the volatiles are depleted, the flame front approaches the particle until oxygen molecules can attack the char directly. The carbon is converted at the surface to CO and the nitrogen to unknown products but probably mostly into NO. In the diffusion flame surrounding the char particle the CO will burn to completion and the NO may possibly be further converted into other products.

In a complete model for the combustion process, each of these regimes should be simulated and the results combined in proper proportions, a problem of prime concern being to determine the relative importance of the various regimes. With respect to fuel nitrogen conversion, this will require a knowledge of how nitrogen is distributed between the volatile fractions and the char. Unfortunately, a good, consistent set of data is not available showing how the fuel nitrogen is distributed among the pyrolysis products. By the use of fragmentary data, however, (752), (753), (754)[*], we have drawn up the distribution diagrams shown in Figures 2 and 3 to give a rough idea of how the N is distributed. It appears that most of the nitrogen in coal will appear in the char so that modeling of char combustion must have highest priority for this fuel. For the case of a residual oil, an appreciable fraction of the nitrogen will appear in the char, so that even here the combustion of the pyrolyzed residue will be important. A certain fraction of the nitrogen from the coal combustion, and even more from residual oils, is volatilized, however. It is expected that this volatile matter will be strongly pyrolyzed as a

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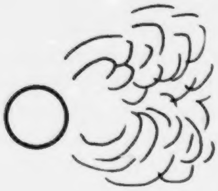
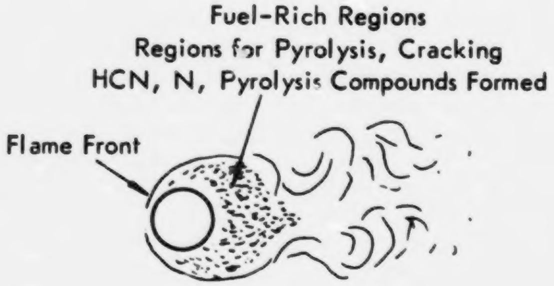
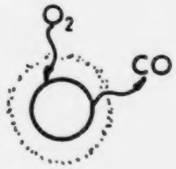
[*] Reference numbers quoted are the acquisition numbers in the CODEN-oriented list of references given in Appendix II.



A. Totally Detached Flame. Rapid Mixing, Rapid Volatilization


Fuel-Rich Regions
Regions for Pyrolysis, Cracking
HCN, N, Pyrolysis Compounds Formed
Flame Front

B. Attached, Diffusion Flame. Pyrolysis Occurs in Fuel-Rich Region
Char is Being Formed



C. Char Burn-Out. Surface Combustion Occurs when Volatiles have Been Driven Out. CO Formed as Result of Surface Reaction of Carbon and O_2. This CO Burns Externally to the Solid Particle in a Diffusion Flame.

Figure 1. THREE REGIMES OF PARTICLE OR DROPLET COMBUSTION

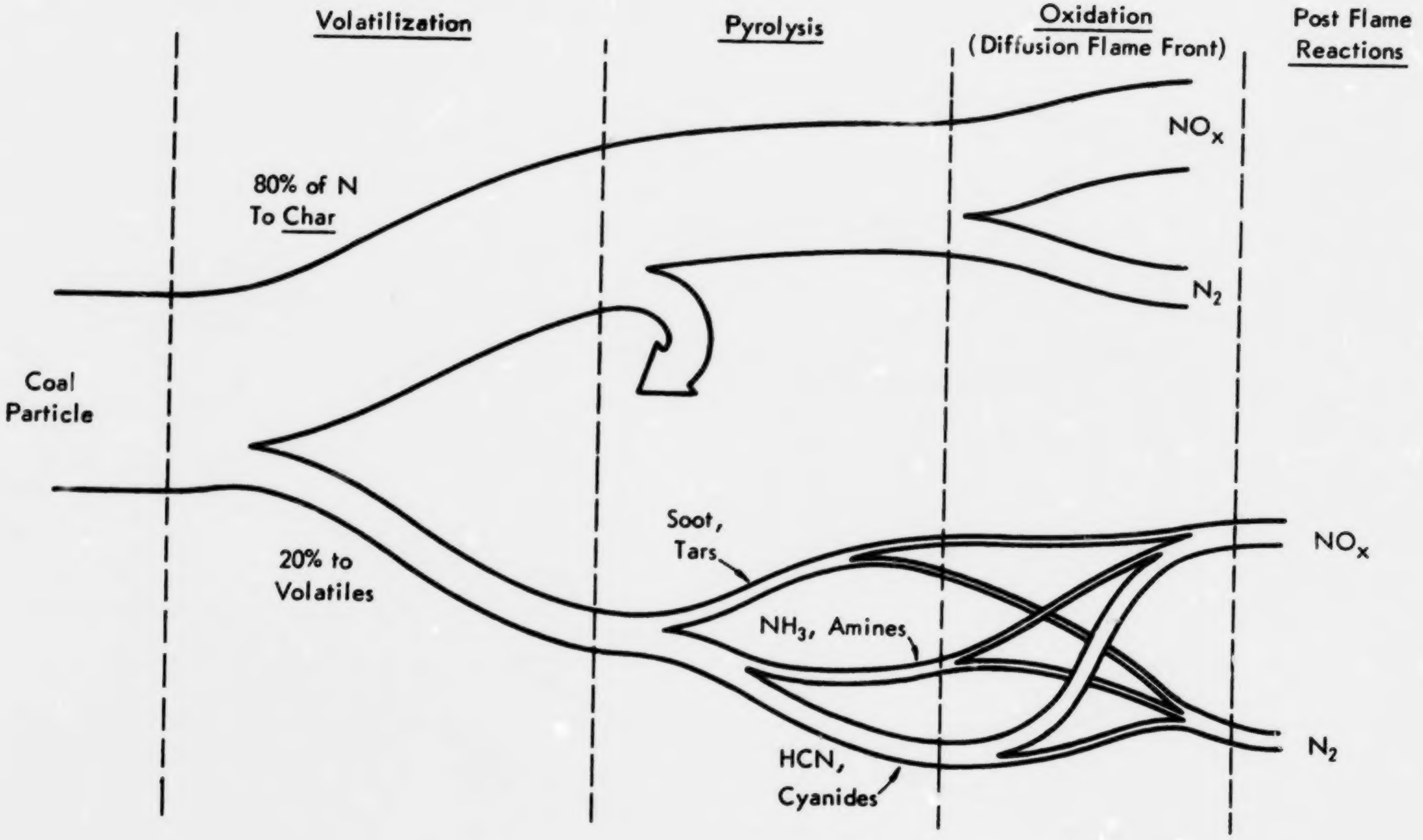

Volatilization
Pyrolysis
Oxidation
(Diffusion Flame Front)
Post Flame
Reactions
80% of N
To Char
Coal
Particle
20% to
Volatiles
Soot,
Tars
NH$_3$, Amines
HCN,
Cyanides
NO$_x$
N$_2$
NO$_x$
N$_2$

Figure 2. TENTATIVE DIAGRAM SHOWING PATHS TAKEN BY FUEL NITROGEN IN COAL COMBUSTION

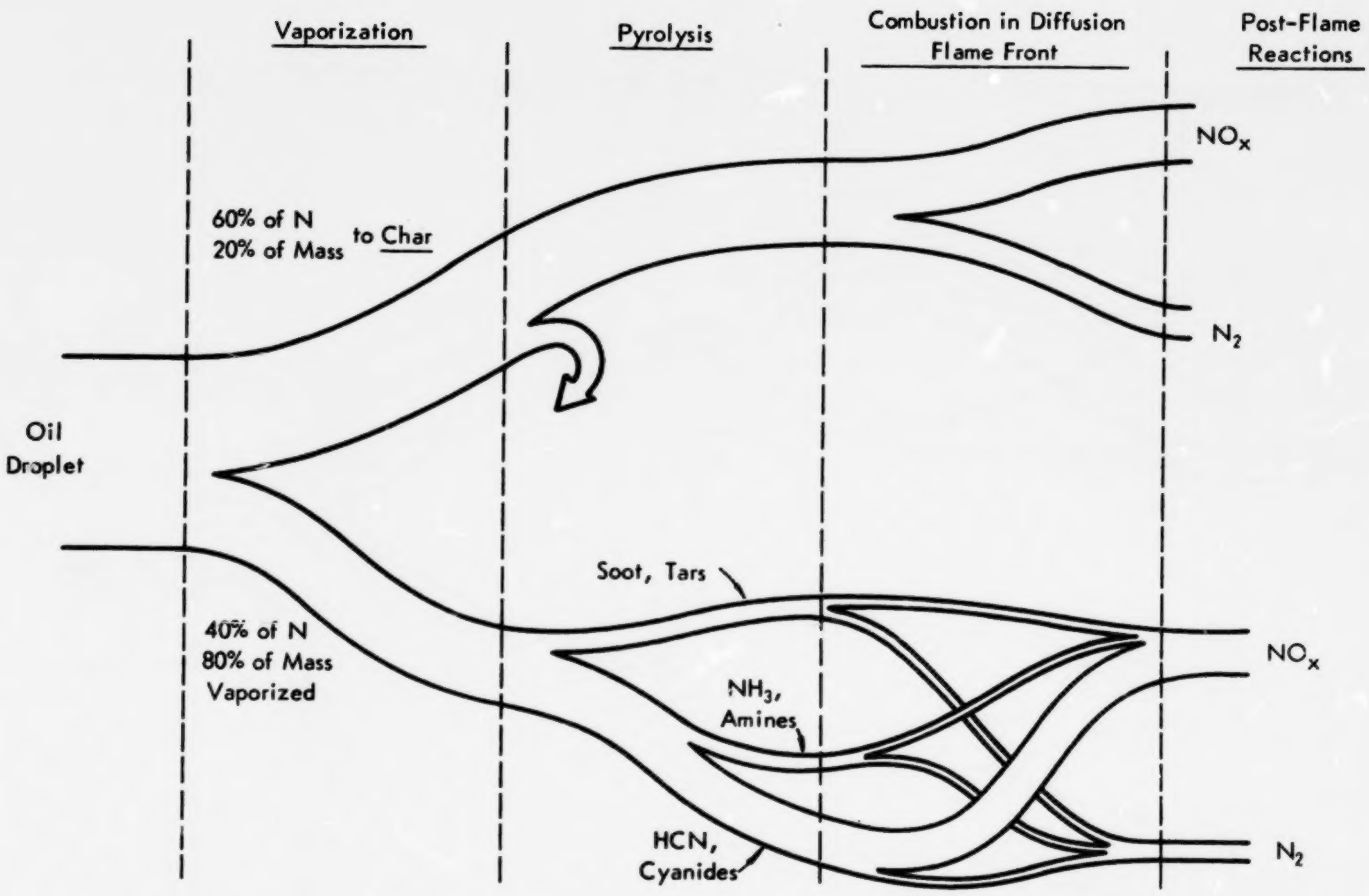

Vaporization
Pyrolysis
Combustion in Diffusion Flame Front
Post-Flame Reactions
Oil Droplet
60% of N
20% of Mass to Char
40% of N
80% of Mass
Vaporized
Soot, Tars
NH_3, Amines
HCN, Cyanides
NO_x
N_2
NO_x
N_2

Figure 3. TENTATIVE DIAGRAM SHOWING PATHS TAKEN BY FUEL NITROGEN IN RESIDUAL OIL COMBUSTION

vapor to form primarily organic cyanides and lesser amounts of ammonia and related compounds.

For simplicity we have worked mainly with regime 2 mentioned above and have concentrated our attention on the volatile nitrogen. Nevertheless, some of the models can be applied to the later stages of char combustion also. Examples are the "reburning" of NO and the conversion of sulfur compounds beyond the stage of oxidation represented by SO_2.

Method of Documenting Arrhenius Constants for Reactions

In the course of this work, a great many reactions were considered, and for some of these several different sets of Arrhenius rate parameters were used. Appendix I documents the reactions and rates by assigning a distinct name to each reaction with its sets of forward and reverse rate constants.

Equilibrium Considerations

Combustion normally is carried out with an excess of air. If chemical equilibrium were reached under such conditions, very low concentrations of pollutants other than NO, NO_2, SO_2, and SO_3 would be present in the combustion products. Since some promising techniques of combustion modification envision the use of less than the stoichiometrically required air, it appears worthwhile to review the equilibrium concentrations in combustion gases for both fuel-rich and fuel-lean conditions. In addition to the major species, we are interested in SO_2, SO_3, COS, CS_2, NO, NO_2, O, OH, H, H_2S, SO, HCN, and C_2N_2.

Two families of calculations were made using the Shell Program CHEMEQ (Chemical Equilibrium). Equilibrium compositions are determined by minimization of the system free energy using a modification of Hopf's method (755). Thermochemical data were taken from the JANAF (756) tables.

The first set of calculations omitted the cyanides but included all the other species mentioned above. Calculations were made for 1200°K and 1800°K for an input composition resulting from burning CH_4 with excess air and then progressively enriching the inlet mixture by adding various amounts of CO. Table 1 shows some of the results. It can be seen that the mole fractions of CS_2 are well below 1 ppm but that COS, H_2S, and SO are near or slightly above the 1 ppm level in some cases.

Table 1. EQUILIBRIUM COMPOSITION AT 1200°K

CO Added	.001	.04
O_2	$.174 \times 10^{-1}$	$.111 \times 10^{-11}$
N_2	.751	.735
CO_2	.116	.149
SO_2	$.967 \times 10^{-3}$	$.945 \times 10^{-3}$
H_2O	.115	.111
SO_3	$.325 \times 10^{-4}$	$.254 \times 10^{-9}$
CO	$.154 \times 10^{-7}$	$.249 \times 10^{-2}$
COS	$.710 \times 10^{-21}$	$.176 \times 10^{-5}$
CS_2	$< 10^{-34}$	$.480 \times 10^{-11}$
NO	$.614 \times 10^{-4}$	$.484 \times 10^{-9}$
NO_2	$.408 \times 10^{-6}$	$.257 \times 10^{-16}$
O	$.325 \times 10^{-8}$	$.259 \times 10^{-13}$
OH	$.177 \times 10^{-5}$	$.490 \times 10^{-8}$
H	$.208 \times 10^{-10}$	$.724 \times 10^{-8}$
H_2	$.109 \times 10^{-7}$	$.132 \times 10^{-2}$
H_2S	$.169 \times 10^{-19}$	$.315 \times 10^{-4}$
SO	$.497 \times 10^{-11}$	$.608 \times 10^{-6}$

The second family of calculations was designed to determine the equilibrium concentrations of HCN and cyanogen. Hydrogen cyanide has been detected in cigarette smoke (415) and in the products of combustion of CH_4 with NO_2 as an oxidizer (757). It is also found in large concentrations in the products of pyrolysis of nitrogen-containing fuel components such as pyridine (372), (363). Results of equilibrium calculations are reported here for a simulated No. 2 fuel oil burned under fuel-rich conditions. The overall stoichiometry for the major species is represented by

CASE A - 90% of theoretical air

$$CH_{1.2} + 1.17\ O_2 + 4.414\ N_2 \longrightarrow 0.6\ H_2O + 0.74\ CO_2 + 0.26\ CO + 4.414\ N_2$$

CASE B - 80% of theoretical air

$$CH_{1.2} + 1.04\ O_2 + 3.924\ N_2 \longrightarrow 0.6\ H_2O + 0.48\ CO_2 + 0.52\ CO + 3.924\ N_2$$

To check the results, the calculations were made by three different methods.

Method I

Assuming that the concentrations of N_2, CO, CO_2, and H_2O are fixed, we consider the reaction

$$HCN + \frac{3}{2}CO_2 \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}H_2O + \frac{5}{2}CO \qquad (2)$$

The equilibrium partial pressure, P_{HCN}, of HCN, in atmospheres is then given by

$$P_{HCN} = \frac{P_{H_2O}^{1/2}\ P_{N_2}^{1/2}\ P_{CO}^{5/2}}{P_{CO_2}^{3/2}\ K_{P_{react}}} \qquad (2a)$$

Values of equilibrium constants were taken from the JANAF tables and inserted into equation 1. Results are shown in Table 2 and are plotted in Figure 4. It appears that equilibrium HCN concentrations are well below the ppm range. The high reported values of HCN in combustion products are probably not equilibrium-limited but rather rate-limited.

Method II

The Shell Development program CHEMEQ was used on the six-species system N_2, CO, CO_2, H_2O, O_2, HCN. For the case of a fuel gas corresponding to 90% of theoretical air, the equilibrium O_2 and HCN concentrations are shown in Table 3.

Method III

Same as Method II, except that 16 components were considered. Results are shown in Table 4.

The three methods give essentially the same results. When the full 16 species are considered, there is a significant shift in the concentrations of the major species, N_2, CO, CO_2, and H_2O. This explains the slightly different HCN concentration obtained when using this method.

Table 2. EQUILIBRIUM FOR REACTION

$$HCN + \frac{3}{2}CO_2 \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}H_2O + \frac{5}{2}CO$$

	P_{HCN}, Atmospheres	
	Percent of Theoretical Air	
Temp, °K	80	90
2000	.74149979-08	.61330169-09
1900	.85824439-08	.70986227-09
1800	.10130031-07	.83786471-09
1700	.12193009-07	.10084957-08
1600	.15209365-07	.12579814-08
1500	.19661250-07	.16262011-08
1400	.26583438-07	.21987420-08
1300	.38072490-07	.31490127-08
1200	.58426704-07	.48325295-08
1100	.98312956-07	.81315601-08
1000	.18604207-06	.15387720-07

Table 3. EQUILIBRIUM FOR SIX-COMPONENT SYSTEM CALCULATED BY CHEMEQ-90% OF THEORETICAL AIR SIMULATED NO. 2 FUEL OIL

Feed Input Composition		Equilibrium Mole Fractions at			
Species	Mole Frac	1000°K	1400°K	1800°K	2000°K
N_2	.7340+00	.7340+00	.7340+00	.7340+00	.7340+00
CO	.4320-01	.4320-01	.4320-01	.4320-01	.4323-01
CO_2	.1230+00	.1230+00	.1230+00	.1230+00	.1230+00
H_2O	.9977-01	.9977-01	.9977-01	.9977-01	.9977-01
O_2	.0000	.2960-19	.7684-11	.3376-06	.1392-04
HCN	.0000	.1517-07	.2166-08	.8233-09	.6071-09

Table 4. EQUILIBRIUM FOR 16-COMPONENT SYSTEM CALCULATED BY CHEMEQ 90% OF THEORETICAL AIR-SIMULATED NO. 2 FUEL OIL

Feed		Equilibrium Mole Fractions at			
Species	Mole Frac	1400°K	1600°K	1800°K	2000°K
N_2	.7340+00	.7340+00	.7340+00	.7340+00	.7338+00
CO	.4320-01	.3299-01	.3505-01	.3638-01	.3739-01
CO_2	.1230+00	.1332+00	.1312+00	.1298+00	.1288+00
H_2O	.9977-01	.8957-01	.9167-01	.9291-01	.9363-01
O_2	.0000	.1545-10	.5478-08	.5306-06	.2040-04
HCN	.0000	.9284-09	.6394-09	.4766-09	.3818-09
C_2N_2	.0000	.7671-19	.8259-19	.8700-19	.9266-19
O	.0000	.3684-11	.1063-08	.8776-07	.2992-05
H	.0000	.4909-06	.4903-05	.2956-04	.1254.03
OH	.0000	.8389-07	.2120-05	.2614-04	.1942-03
HCHO	.0000	.3036-09	.2260-09	.1789-09	.1497-09
NO	.0000	.6551-08	.3260-06	.6833-05	.7756-04
NO_2	.0000	.4018-15	.2022-12	.2576-10	.1235-08
N_2O	.0000	.3507-12	.1661-10	.3379-09	.3771-08
NH_3	.0000	.7760-07	.3032-07	.1458-07	.8199-08
H_2	.0000	.1021-01	.8151-02	.6831-02	.5957-02

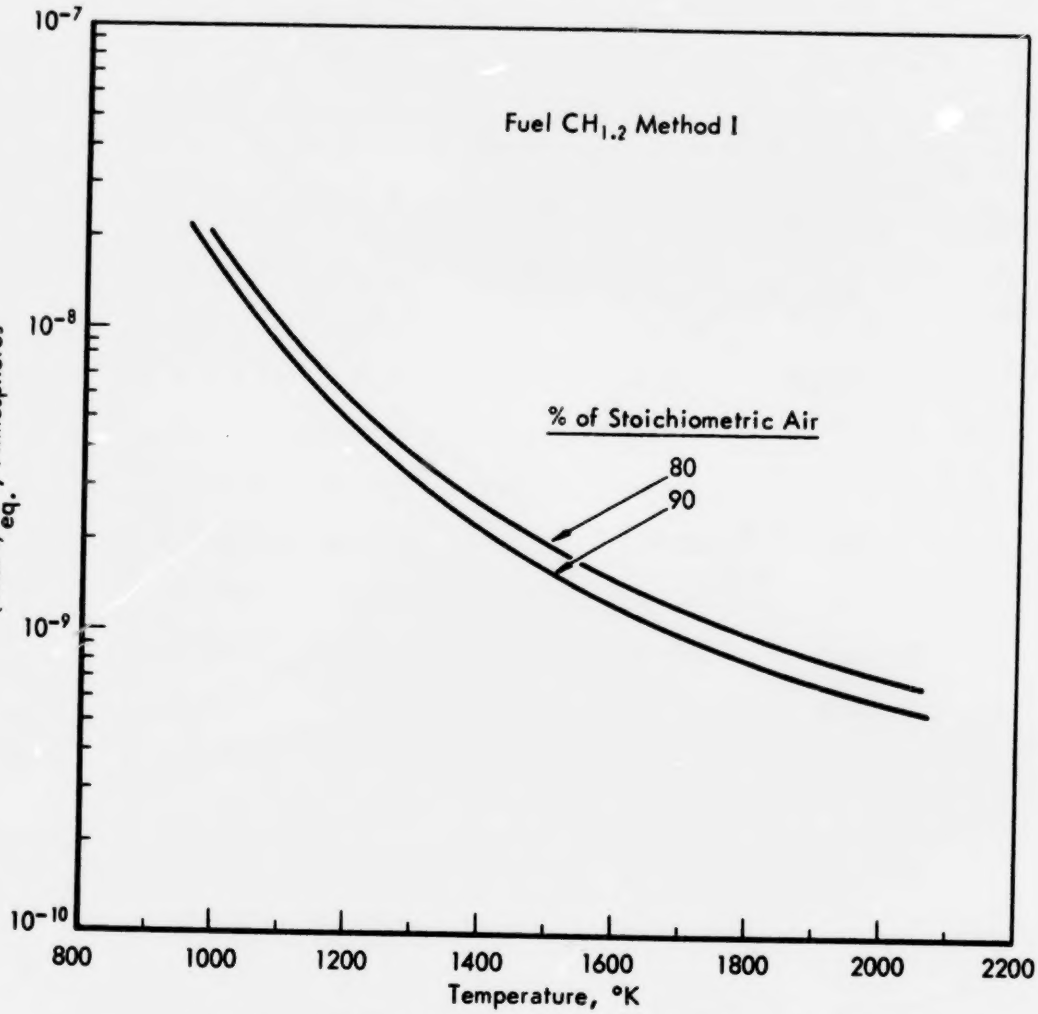


Figure 4. EQUILIBRIUM HCN IN COMBUSTION GASES

Literature Review

In order to formulate critical questions suitable for study by computer simulation of chemical mechanisms, the literature was reviewed giving special attention to pyrolysis of nitrogen compounds, combustion of nitrogen and sulfur compounds, and mechanisms affecting the formation and breaking of the chemical bonds C≡N, N-H, N≡N, and N=O. The literature is very large and cannot be reviewed in detail here. To facilitate citation of references, we have adopted the CODEN system of ASTM (758) used, for example, in Hochstim's (759) review of the kinetics of elementary reactions. Appendix II gives a complete listing of all the pertinent references found, alphabetized by author, periodical, and acquisition number.

Experimental Data on Fuel Nitrogen Conversion in Oil and Coal

Summaries of experimental data on the influence of fuel nitrogen are available in the Esso Report (797) and in papers by Martin and Berkau (790), Turner et al (Esso) (791), and Fine et al (MIT)(798). In this section, we review the literature with the following questions in mind:

(a) What is the effect of fuel N in coal combustion?

(b) What is the effect of fuel N in oil combustion?

(c) Can the NO formed by fixation be separated from that coming from chemically bound N?

(d) What is the effect of excess air on fuel N conversion?

(e) What is the effect of nitrogen level, fuel type, and burner and furnace design?

(f) What is the effect of the type of compound containing the nitrogen?

There are two contrasting opinions on the effect of fuel nitrogen in coal combustion. One, supported by Bartok et al (797), maintains that the nitrogen in coal contributes significantly to NO_x under most firing conditions. Data from a fluid bed combustor with argon/O_2 substituted for air taken by Jonke et al (799) show conclusively that at low temperatures the NO_x is high, comparable to conventional boilers, and is essentially all derived from the nitrogen in the fuel. The other view, proposed by Sarofim and his co-workers at MIT (798) views fluid bed combustion as representative of a premixed system (reaction controlled) which, by analogy, will have a high conversion of CBN* to NO_x, while normal pulverized coal combustion resembles a diffusion flame in which pyrolysis precedes combustion and prevents conversion of CBN to NO_x. To support their view, they present data which indicate that methylamine when burned in a diffusion flame will give a 10% conversion to NO (independent of nitrogen content) compared to an 80% to 40% conversion to NO when burned in a premixed flame. Incidentally, Sarofim and co-workers (798) find that with no CBN in the fuel their diffusion flame had five times the NO_x of their premixed flame. Interestingly, this trend is contrary to boiler experience as reported by Foster Wheeler (800) which shows the reverse trend. (Off-stoichiometric combustion which is known to reduce NO_x can be viewed as a change from a more to a less premixed condition). This suggests that the comparison of Sarofin et al between

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* CBN = Chemically Bound Nitrogen

CBN conversion in premixed and diffusion flames may not be applicable to the real situation prevailing in boilers and furnaces.

In oil combustion there appears to be little doubt that fuel nitrogen contributes heavily to NO_x emissions. This was shown by Martin and Berkau (790) who burned No. 2 fuel oil to which was added various nitrogen compounds. The Esso Report (797) also shows significant increases of NO_x with increasing weight percent nitrogen in fuel oil, although there the comparison is between two different No. 6 oils in the same boiler (175 MW to 480 MW). In a further study with No. 2 fuel oil with CBN additive, Esso confirmed (qualitatively) the results of Martin and Berkau, and with No. 6 oils of different nitrogen contents again confirmed that for a given burner and boiler design nitrogen oxide emissions depend directly on the CBN content of the fuel. They measured 450 ppm with 0.77% N, 320 with 0.31% N, 290 with 0.25% N, and 120 with 0.03% N, on a Cleaver Brooks 50 hp boiler and on a 250 MW utility boiler. Unpublished Shell data on refinery furnaces, boilers, and small oil field steam generators firing fuel oils of various CBN contents is in agreement with Esso's findings. Shell measured 450 ppm with 0.78% N oil against 30 ppm on gas for a simple gun-fired unit with no preheat and poor mixing. On a wide variety of tests on boilers, Shell found that oil flame temperatures (measured by a sodium injection, light emission technique) were, in general, cooler than gas flames, that the data could be correlated by assuming that between 30 and 40% of the CBN was converted to NO_x and that oil flames fix only 20% to 40% as much N_2 from the air as equivalent gas flames of the same heat release. For a 225 M lb/hr steam boiler, Shell found that a low nitrogen oil (0.37% N) gave 252 ppm NO_x or 122 lb/hr at 21.5% excess air, while gas firing (refinery gas) produced 381 ppm or 155 lb/hr at 16.5% excess air. Esso also reported that for large utility boilers gas flames could give higher NO_x than oil. From this data we conclude that (1) NO_x emissions from oil flames depend strongly on CBN content of fuel and (2) oil flames fix less nitrogen from air than gas flames with preheat and good mixing.

The effect of excess air on NO_x emissions from oil flames both with and without specified CBN contents has been well documented by Bartok et al (797), by Turner et al (791), and by Martin and Berkau (790). In each case, NO_x increases with excess air although Turner found this increase was small for excess air levels between 10 and 80%. Shell data for 0.79% CBN indicate 150 ppm (corrected to 3% O_2) at zero percent excess air (with smoke and CO emissions) and 600 ppm (corrected to 3% O_2) at 70% excess air. Turner went further substoichiometric on Esso's Cleaver Brooks boiler burning a residual oil containing 0.35% CBN and obtained 300 ppm at 10% excess air, 200 ppm at -10% excess air, and 40 ppm at close to -30% excess air. All the data shows that for fuel oils containing CBN the total ppm increases as excess air increases.

It is useful to examine techniques used to separate the thermal NO_x from the CBN derived NO_x. In their experiments with No. 2 oil doped with CBN compounds, Martin and Berkau assumed that at a given excess air the thermal NO in all their runs was equal to that produced in the run with no additive. In using this method, care must be taken not to change the fuel properties, such as surface tension, viscosity, etc., affecting drop size and thermal NO. For example, 2% N as quinoline requires that compound to be 18% of the total fuel. Turner et al used a different approach. They hypothesized that flue gas recirculation (FGR) reduced only thermal NO and supported this by showing that 30% recycle reduced NO from No. 2 fuel oil containing 0.03% N to 40 ppm both with high and low atomizing air and that with added fuel nitrogen FGR reduced NO_x by the same amount, 80 ppm. The resulting NO after 30% recycle from the 0.03% fuel oil was exactly the amount that would be obtained from 100% conversion of CBN. They further strenghthened their arguments by showing that for residual fuel oils the reduction of NO obtained by FGR was independent of CBN content, although it was a strong function of type of fuel (No. 6 or No. 2). Their method may be valid for fuel oils in their boiler, but it has been shown by Breen, et al (801) and others that for gas firing (containing, presumably, no CBN) 30% FGR will effect only a 75% reduction in a utility boiler and [by Lange (544)] a 80-90% reduction in a laboratory burner. Therefore, the assumption that 30% FGR eliminates all thermal NO may not always be valid.

The effect of nitrogen content on CBN conversion to NO was studied by Turner who showed, using his method to separate thermal and fuel NO, that for residual fuel oil the conversion decreased from 60% at 0.2% CBN to 40% at 0.4 and greater percent CBN in the fuel. This agrees roughly with the results of Martin and Berkau who observed the same trend in their doped No. 2 oil. Turner, in his experiments with No. 2 fuel oil, found higher conversion than did Martin, and higher than he got with No. 6 oil. The conversion of CBN to NO_x is therefore also a strong function of nitrogen content, of type of fuel, and of heater and burner type (as well as of excess air, as described above). In some tests run by Shell, it was found that when the same fuel containing 0.78% N was burned in very similar heaters, but with different burners, the NO_x was 543 ppm for one burner against 300 ppm for the other, at approximately the same excess air. Further experiments by Shell showed that for a given burner increasing the atomization rate increased the NO by more than the amount emitted by a gas flame of the same heat release. It is not clear, however, whether this increase was due to increases in thermal NO or fuel NO or both. Shell's studies indicate that old, crude burners with inefficient atomization tend to give lower NO_x than more modern burners, on the same high nitrogen fuel and at the same excess air. Data in the Esso Report also indicate that at a given fuel nitrogen content, different boilers give widely different NO_x, with tangential firing giving the lowest NO_x emissions. Further discussions with Combustion Engineering, Inc., disclosed that they had measured only 59 ppm NO_x while burning 0.25% N fuel oil in a 500 M lb/hr steam boiler. If this is true, this would indicate a breakthrough in NO_x control. It is not at all clear why tangential firing should have so much lower fuel nitrogen conversion. Possibly the explanation lies in lower combustion intensity.

The effect of the nature of the nitrogen compound has been examined by Martin and Berkau and by Turner et al. Martin and Berkau found that quinoline (C_9H_7N) gave lower conversions than piperidine ($C_5H_{11}N$) and pyridine (C_5H_5N). The latter two gave identical results. Turner found little influence of additive boiling point on NO_x in a series of tests with twenty different nitrogen compounds in No. 2 fuel oil. Only when the additive boiling point fell below 100°C did the conversion to NO_x drop markedly. Turner attributed this to loss in handling, but the effect may be real.

It is worth mentioning the results of the work by Bienstock (802) et al in an experimental pulverized coal furnace. The coal had a nitrogen content of 1.3%. At 22% excess air, they obtained 600 ppm NO_x emissions. Reduction of excess air to stoichiometric reduced NO_x to 100 ppm. Two-stage air was also very effective in NO_x reduction. The surprising thing about their data is that in each case there was a substantial reduction of NO_x from the flame exit to the stack. This had not been observed before. Their data is shown in Figure 5 where the abscissa is temperature which was measured simultaneously at their sampling point. Although the oxygen content changed from position to position, indicating dilution, this change was not large enough to influence the measured ppm of NO_x.

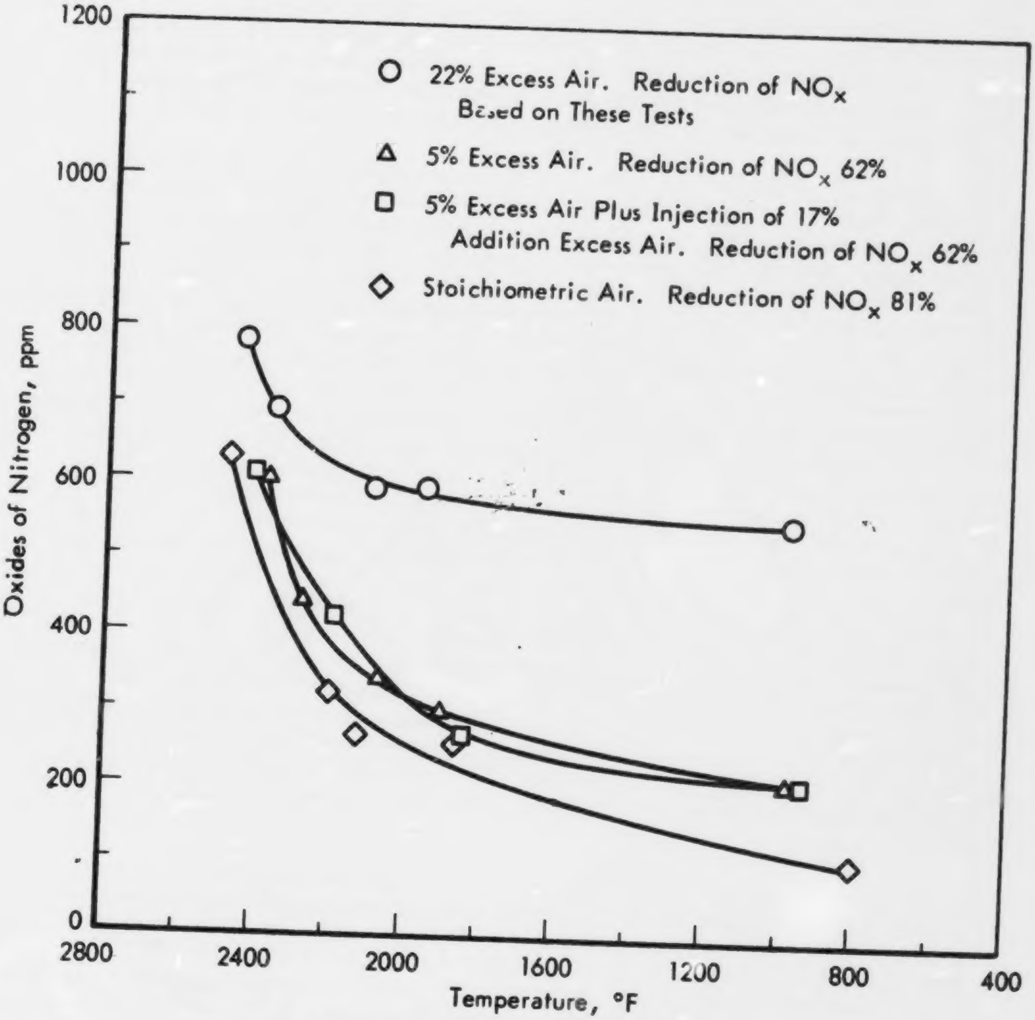


Figure 5. NO_x CONCENTRATION AS A FUNCTION OF EXCESS COMBUSTION AIR

Combustion of Ammonia

Ammonia is the simplest fuel molecule with chemically bound nitrogen. It may also be formed in the pyrolysis of the more complex fuel molecules containing N. For example (760), about 16% of the nitrogen in coal appears as gaseous ammonia during conventional coking operations. Ammonia, as the parent compound, may also serve as a partial model for the combustion of amines. The combustion of ammonia has also been studied more thoroughly than that of any other fuel nitrogen compound. This section gives a brief literature review of ammonia combustion.

It is by no means clear what combustion conditions lead to high conversions to N_2 and what conditions lead to low conversions; data of both types have been reported. Several studies indicate that conversion to NO_x is high under fuel-lean conditions [Husain and Norrish (387), Bull (765), Bradley et al (762), Fenimore and Jones (763), Drummond and Hiscock (764), MacLean and Wagner (765), Sutton and Starkman (766), and unpublished studies in Shell laboratories]. Under fuel-rich conditions, several studies show low conversions to NO_x (Fenimore and Jones, Sutton and Starkman). In contrast to this rather simple picture, Andrews and Gray (767) in a laminar flame experiment obtained not more than 12% conversion to NO_x under both fuel-lean and fuel-rich conditions. Also, experiments (unpublished) in Shell laboratories show a relatively high conversion (37%) at extremely fuel-rich conditions (39% of theoretical air). In this experiment, the flame temperature was kept artificially high.

The most interesting phenomena described in the literature on ammonia combustion are (1) early formation and subsequent reduction of NO in fuel-rich flames, (2) decomposition of NH_3 to N_2 and H_2 before O_2 is encountered, and (3) the overall mechanisms of combustion. Fenimore and Jones found that NO was formed as an intermediate and then destroyed. They proposed that NH_2 was the reducing agent:

$$NO + NH_2 = N_2 + \cdots \qquad (3)$$

They also found ammonia in the residual gas. MacLean and Wagner found that NO was produced in small amounts and decayed slowly and that no residual NH_3 appeared in the burned gas of fuel-rich flames. Similarly, no NH_3 passed undecomposed through the rich flames of Gray, McKniven, and Smith (768) or of Bull (765). Both of these investigators found N_2O as an intermediate. Furthermore, MacLean and Wagner found that N_2O was formed where NO was being produced most rapidly.

Drummond and Hiscock (764), in a shock tube study, found substantial reduction of NO and conjectured the reaction:

$$NO + NH = N_2 + OH \qquad (4)$$

Almost complete decomposition of ammonia to N_2 and H_2 was observed in the diffusion flame experiments described by Gaydon and Wolfhard (769), (770). However, their flame was very hot since they burned with oxygen. Peaks in NH and NH_2 radicals were observed about 1 mm from the flame front on the rich side where the temperature was about 2500°K suggesting that most of the ammonia was pyrolyzing there.

As regards overall mechanisms for ammonia combustion, the two leading contenders are shown in Table 5. Mechanism I, due to Husain and Norrish, is analogous to the most widely accepted mechanism proposed for CH_4 combustion at high temperature. [See Fristrom (775)]. First, a free radical, e.g., OH, abstracts H from NH_3. After that, the key step is in the four-center reaction:

$$NH_2 + O_2 = HNO + OH \qquad (5)$$

The HNO subsequently goes to NO. In their flash photolysis experiments, Husain and Norrish found OH and NH after delays of about 500 microsec but could not detect HNO. This weakens somewhat the credibility of their mechanism. They mention that NH_3 was converted completely to NO! Mechanism II, by Takeyama et al (772), was suggested to explain their shock tube studies. Instead of reaction 5, they propose:

$$NH_2 + O_2 \longrightarrow NH + HO_2 \qquad (6)$$

followed by the four-center reaction

$$NH + O_2 = NO + OH \qquad (7)$$

Thus, they introduce, in a new context, the old controversy about the possible significance of the hydroperoxyl radical, HO_2, in high-temperature combustion. Both of the mechanisms described above predict the formation of large amounts of NO, and neither is able to account for appreciable conversion of NH_3 to N_2. Based on present knowledge, Mechanisms I and II appear equally likely although the failure to detect HNO tells against Mechanism I. Despite this, most investigators prefer I. It would appear that both mechanisms should be expanded to include N_2O as an intermediate. Any useful mechanism should explain the large yields of N_2 and the formation and subsequent decay of NO under fuel-rich conditions. The scheme of Wilde (773) looks promising. It was proposed for the reaction of H_2 with NO and involves HNO as a key intermediate. Wilde obtained good agreement with literature data on the initial rate of the reaction.

We can summarize the discussion of ammonia combustion by the following unanswered questions:

1. What species is responsible for chain branching: HNO, HO_2, or other?
2. What is the role of N_2O; how is it formed and then destroyed?
3. How is NO destroyed in fuel-rich flames?
4. How is the N-to-N bond formed?

Table 5. MECHANISMS OF NH_3 OXIDATION

I. Husain and Norrish (387)

$NH_3 + M = NH_2 + H + M$	1	initiation
$NH_2 + O_2 = HNO + OH$	2	
$OH + NH_3 = NH_2 + H_2O$	3	key depletion
$HNO = H + NO$	4	branching
$HNO + HNO = H_2O + N_2O$	5	
$HNO + OH = H_2O + NO$	6	
$H + HNO = H_2 + NO$	7	

II. Takeyama and Miyama (772)

$NH_3 + M = NH_2 + H + M$	1	initiation
$NH_2 + O_2 = NH + HO_2$	2	
$HO_2 = OH + O$	3	branching
$OH + NH_3 = NH_2 + OH$	4	key depletion
$O + NH_3 = NH_2 + OH$	5	
$NH + O_2 = NO + OH$	6	
$NH + OH = N + H_2O$	7	
$N + O_2 = NO$, etc.	8	
$NH + NO = N_2 + OH$	possibly	

Cyanides and Combustion Using Nitrogen Oxides as the Oxidizer

A number of investigators have studied combustion of hydrocarbons and other fuels supported by the oxidizers N_2O, NO, or NO_2 [Gray et al (777), Myerson et al (778), Patry and Engel (779)]. These studies are of interest for the present problem from another viewpoint, that of the reduction of nitrogen oxides to N_2 by hydrocarbons in flames. In a number of cases detailed information about the final products of reaction is not given. Among the products detected are HCN and formaldoxime (CHO-N=O). For example, Myerson et al find up to 1.1 moles of HCN per mole of propane consumed in the propane-NO_2 flame. Patry and Engel found 70% of the NO, when reacted with methane, went to form HCN at temperatures up to 1100°C.

Fenimore (721), in his study of the "prompt" NO in hydrocarbon flames, was led to postulate the formation of cyanides by reactions like

$$CH + N_2 = HCN + N \qquad (8)$$

$$C_2 + N_2 = CN + CN \qquad (9)$$

Unpublished experiments at Shell have shown appreciable formation of HCN by the reaction of nitrogen plasmas with methane. Bockhorn et al (804) produced large yields of HCN in a staged flame.

Oxidation of HCN

The burning of HCN probably plays a central role in combustion of the pyrolysis products of heterocyclic nitrogen compounds and in the formation of prompt NO by the method proposed by Fenimore. Little is known about the mechanism of combustion of HCN; the best available article appears to be that of Ailliet and van Tiggelen (386). They report burning velocities over a wide range of conditions and discuss briefly the mechanism of combustion. They suggest that the following reactions are important.

$$HCN + H = H_2 + CN \qquad (10)$$

$$CN + O_2 = NCO + O \qquad (11)$$

$$HCN + O = NCO + H \qquad (12)$$

$$NCO + O_2 = CO + NO + O \qquad (13)$$

$$NCO + O = NO + CO \qquad (14)$$

To these must obviously be added the reactions for hydrogen combustion and probably these additional routes for CN formation:

$$HCN + O = OH + CN \qquad (15)$$

$$HCN + OH = H_2O + CN \qquad (16)$$

Possibly N_2 is made by the reaction (724):

$$NCO + NCO = N_2 + CO + CO \qquad (17)$$

Basco (357) has obtained data indicating that

$$CN + O_2 = CO + NO \tag{18}$$

also occurs. For room temperature, Basco gives the rate of reaction 11 as

$$k_f = 4.6 \times 10^{12}\ \mathrm{cm^3/(mole,\ sec)}$$

and he concludes that the rate of reaction 18 is less than 0.15 times the rate of reaction 11.

Other references discussing reactions connected with HCN combustion are (358), (359), (360), (379), (385), (412), (407), (424).

Low-Temperature Mechanisms Involving N-N Bond Formation

The key to understanding the mechanism by which fuel nitrogen is converted partially into N_2 lies in understanding how the N-to-N bond is formed. Possibly, the same reactions are involved as occur in the N_2 fixation process. For example, the Zeldovich cycle

$$N_2 + O = NO + N \tag{19}$$

$$N + O_2 = NO + O \tag{20}$$

or the N_2O cycle

$$N_2 + O + M = N_2O + M \tag{21}$$

$$N_2O + O = NO + NO \tag{22}$$

can function in reverse. However, if these are the only reactions involved, it is difficult to explain how yields of NO_x much lower than equilibrium values can be obtained. In the extensive literature [see, for example, (780)] on reactions of organic nitrogen compounds, several mechanisms forming N-to-N bonds have been discussed. Most of these mechanisms have been studied only at low temperature or in aqueous media and hence may not be directly applicable to flame conditions. Nevertheless, some insight into possible significant flame reactions can be gained from this literature.

Nitrogen gas is formed directly by the reaction of nitrous acid with primary amines [(781), page 160]

$$CH_3NH_2 + HONO = CH_3OH + N_2 + H_2O \tag{23}$$

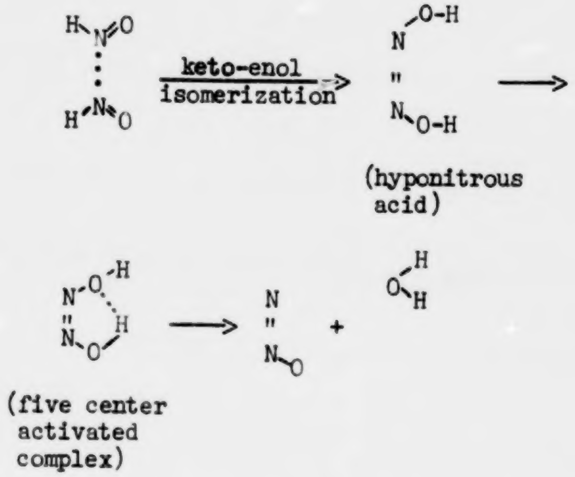
With secondary amines the first product is a nitrosamine

$$(CH_3)_2NH + HONO = (CH_3)_2NNO + H_2O \tag{24}$$

Similar reactions can occur with HNO in place of HONO. For example, Levy (805) in discussing the formation of N_2 in flames of hydrocarbons with NO_2 postulated the reaction

$$HNO + HNO = N_2O + H_2O \tag{25}$$

It is difficult to construct a simple activated complex for this reaction unless several steps are postulated. By analogy with reaction 24 we can, however, picture the following sequence



(26)

Credence is lent to this sequence by knowledge that a standard method for formation of N_2O is by decomposition of hyponitrous acid (805), (803, page 661).

Other methods of forming the N-to-N bond are through linkage reactions similar to 26 but involving more complex molecules. Thus we may have

$$NO + NO + M = N_2O_2 + M \tag{27}$$

$$NO_2 + NO_2 = N_2O_4 \tag{28}$$

$$NO + NH_2 = NH_2NO \text{ (nitrosamine)} \tag{29}$$

$$NH + NH = N_2H_2 \tag{30}$$

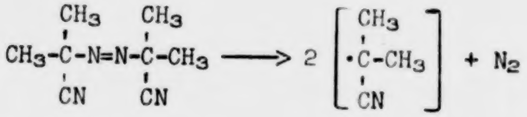
...

Species which possibly might be involved in these linkage reactions are shown in Table 6. On first glance, it seems improbable that these reactions could be important routes for synthesis of N_2. This is shown by considering

$$NO + NO + M = N_2O_2 + M \tag{31}$$

Using the thermodynamic data of Guggenheim (408), together with an estimate of the maximum rate we found rates of the order of 2×10^{-12} g moles/sec cm^3 which is much too slow to explain N_2 formation in furnaces.

Azo compounds, especially the azonitriles (780, page 686), are used widely as free radical sources because of their tendency to decompose yielding molecular N_2 (and a pair of free radicals)



$$CH_3\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3 \longrightarrow 2\left[\cdot\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3\right] + N_2 \qquad (32)$$

It is possible that collision of the two free radicals $(CH_3)_2CN\text{-}N{:}$ could lead in one step to the same products.

Table 6. NITROGEN COMPOUNDS WHICH MIGHT BE INVOLVED IN LINKAGE REACTIONS

N
NH
NH_2
NH_3
NH_2OH
$HONO$
$HONO_2$
N_2O
NO
NO_2
NO_3
N_2O_2
N_2O_3
N_2O_4

N_2O_5
$HNNH$ (diimine)
N_2H_4
$HONNOH$
CN
C_2N_2
HCN
$HCNO$ cyanates
$HNCO$ isocyanates
N_3^- azides
HN_3 hydrazoic acid
$H_2N_2O_2$ nitramide
$H\text{-}C{=}N{\rightarrow}O$ formonitrilioxide
$\text{-}C{=}N{\rightarrow}O$ fulminate radical formonitrile oxide

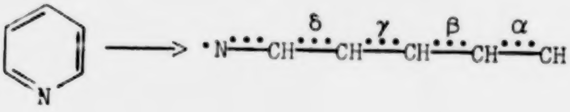
Pyrolysis

In the combustion of liquid droplets, an oxygen-deficient region around the drop will be formed as the vaporized fuel moves outward. Also under fuel-rich combustion, the entire combustion products are deficient in oxygen. Under these conditions simple pyrolysis of the fuel molecules may be important.

It is observed that pyridine is partially decomposed by heat at temperatures above 850°C (372), (363). Products formed are HCN, light gases, and condensation products of the original molecule and hydrocarbon radical fragments.

Quantitative data on rates of cracking of nitrogen compounds are scarce. An approximate idea of the rates can be obtained by comparison with the much more abundant data for pyrolysis of gas oils. Considerable data is available for these materials (boiling range 200°C-400°C) due to commercial interest in olefin manufacture by gas oil cracking (370), (371).

Hurd, Macon, Simon and Levetan (414) summarize the severe pyrolysis of pyridine as follows. "The hetero bond (C-N) in pyridine is the point of initial rupture into diradicals.

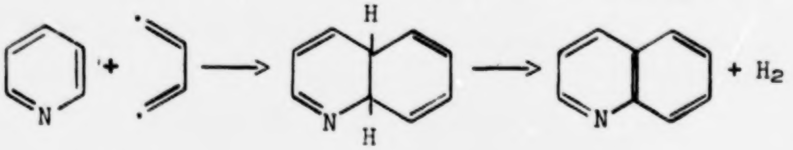


(33)

After this occurs, somewhat random rupture of the other bonds occurs, but rupture at γ and δ should be favored. Rupture at δ leads to HCN and the C_4 diradical

•CH=CH-CH=CH• "

The latter serves to explain the formation of polyaromatic rings, e.g.,



(34)

Ruhemann (784) stated that at 900°C practically complete cleavage of the pyridine ring occurred. Among the gaseous products were HCN, H_2 at 84-86%, CH_4 at 12-14%, and olefins at 1-2%.

A typical value for the first order rate constant for cracking of a normal hydrocarbon of molecular weight of about 225 is

$$k = 10^{14} \exp(-58000/RT) \text{ sec}^{-1}$$

With such a rate, one would expect half of the original molecules to be cracked in about 30 millisec at 1000°K, in 2 microsec at 1500°K, and within 10^{-8} sec at temperatures over 2000°K. This degree of cracking leads to about 4 molecules for each molecule cracked and of these three are lighter than molecular weight 80. In such processes the temperature is lower, the residence time is shorter, and the oil being pyrolyzed is lighter than for the case of combustion of a residual oil in a furnace. Despite the differences, the data can be used as an indication of what molecules will result from pyrolysis. Figure 6 shows the effect of increasing temperature and residence time on product distribution.

Highly aromatic compounds probably behave quite differently, being more refractory and also producing fewer small molecules and more polyaromatic material. Nevertheless, at typical flame temperatures, their life before cracking is probably also quite short compared to the time required for a molecule to diffuse from drop surface to flame front. Pyridine, which is an aromatic compound, decomposes appreciably at 1100°K (363). At such temperatures, nearly all of the material goes to form such larger molecules as quinoline although small amounts of HCN have been detected. In petroleum coking processes, it appears that most of the nitrogen in the fuel stock goes to the coke rather than to the light molecules formed.

Using the fragmentary data on distribution of nitrogen among the various pyrolysis products (753), (754), (760), etc., we have constructed the typical distribution charts shown as Figures 2 and 3. For coal, most of the nitrogen is expected to appear in the char phase and for residual fuel oils a substantial fraction will appear there. If this is so, the details of combustion of the char phase will be very important in governing the fraction of fuel nitrogen converted to NO_x. Good data is urgently needed on this point. Since analysis of nitrogen in coke from coal show of the order of 1% by weight (753), it is obviously fallacious to think of the volatilization as removing most of the nitrogen. Analyses of petroleum cokes also show high nitrogen, up to 3% by weight. However, much less char is made from oils than from coal.

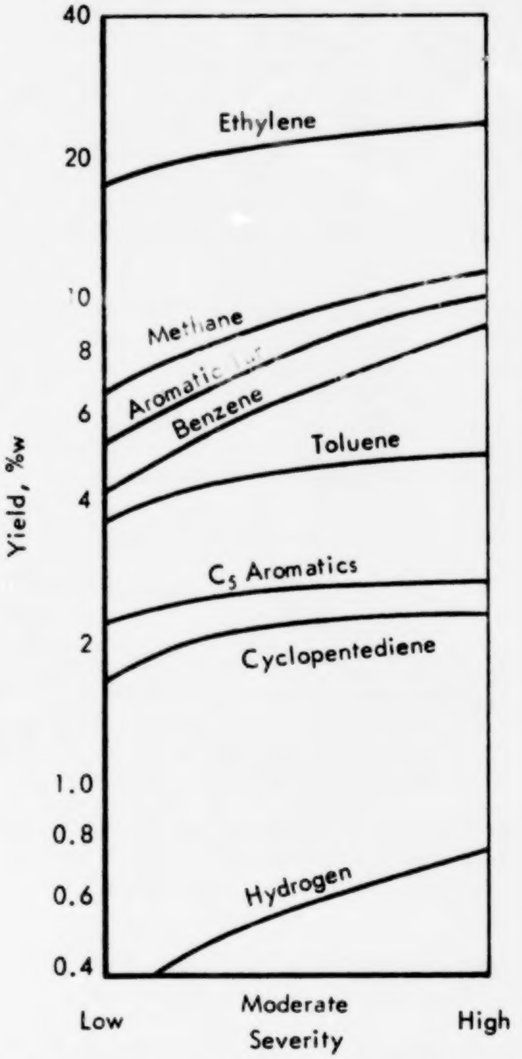


Figure 6. EFFECT OF CRACKING SEVERITY ON PRODUCT DISTRIBUTION IN GAS-OIL CRACKING

From Oil and Gas Journal 74 (Jan. 1971)

Reactions Involving Sulfur

In conventional combustion systems, the presence of sulfur compounds in the fuel can lead to the formation of sulfur dioxide, SO_2, and sulfur trioxide, SO_3. Sulfur trioxide is the more noxious of the two and can lead to corrosion in air preheaters and the formation of plumes. Certain operating conditions that may minimize NO_x formation, such as rapid temperature quench, may cause large amounts of SO_3 to be formed, and may therefore not be practical because of SO_3 (or, more correctly, H_2SO_4) plumes that may violate local air pollution plume opacity regulations. The formation of sulfur trioxide is also of interest because it depends strongly on the higher-than-equilibrium concentration of O atoms in the flame; therefore, its study can give insight into the role of superequilibrium O atoms in the formation of other pollutants, especially that of "prompt" NO. In addition to this, it has been shown that sulfur and nitrogen oxides interact and that synergisms occur in the formation of both pollutants. A significant effort was therefore expended to elucidate the kinetic mechanisms of sulfur trioxide formation and to determine how nitrogen oxides and sulfur oxides interact during and after the flame.

A review of the literature on SO_3 formation has shown that the mechanisms of oxidation can be divided into two categories--homogeneous and heterogeneous. Homogeneous mechanisms include those reactions occurring both in the flame and in the high-temperature reaction zone in the flue gas beyond the flame. Heterogeneous mechanisms involve both suspended fly ash and furnace deposits. In this study, the heterogeneous mechanisms have been considered only insofar as they affect data and, thus, may mislead investigators of the homogeneous mechanism.

The relative importance of the homogeneous and the heterogeneous mechanism of SO_3 formation almost certainly must depend on the particular furnace, fuel, operating conditions in question, but some (611), 612), (338) have insisted that one or the other was the major source.

Studying the effects of SO_2 injection in various regions of a pilot-plant-size steam boiler on corrosion probe measurements, Andersen and Manlik (613) concluded that roughly equal amounts of SO_3 were being formed in the flame, the high temperature gas region beyond the flame, the flues, and the stack. All of this seems to indicate that none of the mechanisms can be ruled out a priori in any situation.

Before discussing the various mechanisms involved, an examination of the SO_x equilibria in flue gas systems is in order. This point was examined using the Shell program CHEMEQ. The following species were considered to be present in the gas:

O_2, N_2, CO_2, H_2O, CO, COS, CS_2, SO, SO_2, SO_3,
H_2SO_4, H_2S, NO, NO_2, NO_3, O, OH, H, H_2

The input mixture was assumed to contain 12% CO_2, 12% H_2O, 0.1% SO_2, and various levels of O_2 with N_2 adjusted to make up 100% gas composition. The JANAF tables were used as the source of thermodynamic data. **Figures 7 and 8 show that at high** temperatures SO_2 is favored, at low temperatures gaseous H_2SO_4 is favored, with the maximum SO_3 levels occurring about 700°K.

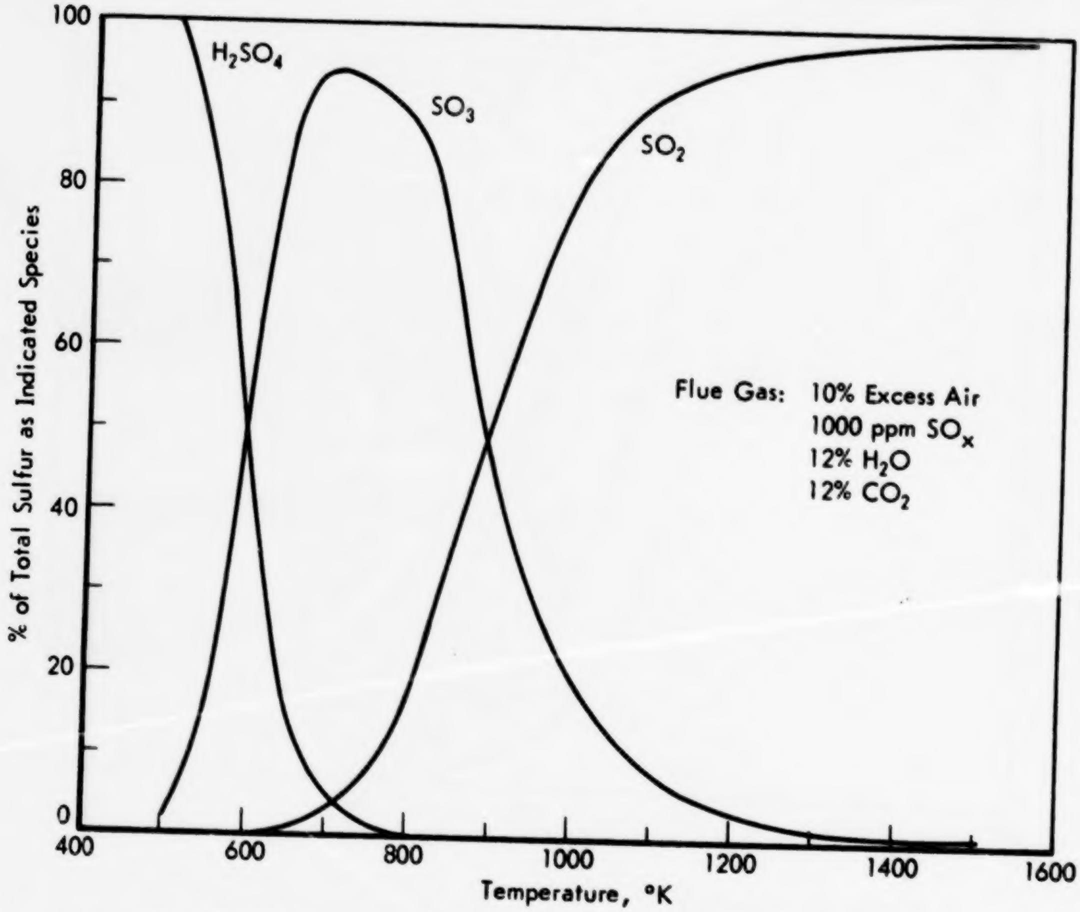


Figure 7. EQUILIBRIA OF SULFUR SPECIES IN A 10% EXCESS AIR FLUE GAS

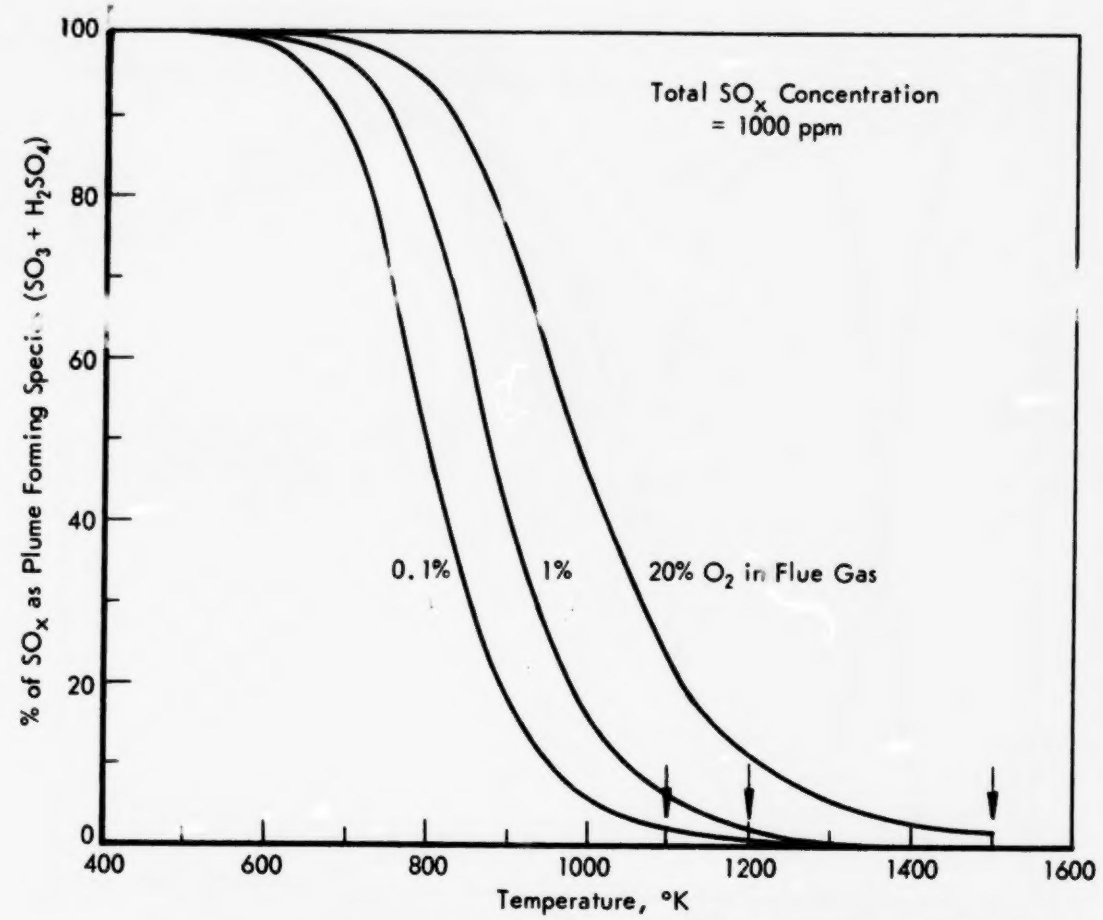


Figure 8. EQUILIBRIUM LEVELS OF PLUME FORMING SPECIES

If equilibrium were achieved, almost all the sulfur emitted at stack temperatures would be in the form of SO_3 or H_2SO_4. In fact, less than 20% of the sulfur is emitted in this form. Evidently we are dealing with a case of frozen equilibrium, where a moderate amount of SO_3 is formed at the high temperature region where it is not favored thermodynamically and that as the temperature is dropped a certain concentration is frozen in. This is demonstrated in Figure 9, taken from Hedley (313). This situation is distinguished from that of NO_x in that locally in the flame the SO_3 is formed in superequilibrium amounts, and then decays, while NO_x seldom reaches equilibrium in the hot flame zone when its formation is by fixation only. (Recent experimental data on ammonia combustion, however, has shown that there NO can be formed in amounts vastly exceeding equilibrium at the peak flame temperature). Equilibrium considerations in pollutant formation can, therefore, be grossly misleading.

The basic mechanism controlling the level of SO_3 in flames involves oxidation of SO_2 by atomic oxygen (612), (345), (614) and decomposition of SO_3 by reaction with atomic oxygen or hydrogen

$$SO_2 + O + M \longrightarrow SO_3 + M \qquad (35)$$

$$SO_3 + O \longrightarrow SO_2 + O_2 \qquad (36)$$

$$SO_3 + H \longrightarrow SO_2 + OH \qquad (37)$$

where M is any third body. This mechanism has been shown (615), (333) to occur just beyond the visible flame, after the combustion reactions are complete and before the free-radicals levels have decayed. Analysis of available rate data for 35 yields (see Table 8)

$$k_{35} = 2.0 \times 10^{16} \exp(-1070/RT) \text{ cm}^6/\text{mole}^2/\text{sec}$$

Nettleton and Stirling (616) report

$$k_{36} = 10^{12} \text{ cm}^3/\text{mole/sec at } 2150°\text{K}$$

and Merryman and Levy (617) find

$$k_{36} = 2.8 \times 10^{14} \exp(-12000/RT) \text{ to } 6.5 \times 10^{14} \exp(-10800/RT)$$

No estimates for the rate of 37 have been found, but Fenimore and Jones (333) estimate that the ratio of k_{35} to the largest of the k_{36} or k_{37} is of the order of 10^4 cm^3/mole. Therefore, the slowness of the SO_3 decay reactions coupled with the high levels of atomic oxygen in the flame can lead to very high SO_3 levels. In fact, observations in oil and gas fired (614), (616) units indicate that maximum SO_3 levels can be higher than those predicted by the SO_2-O_2-SO_3 equilibrium. In the systems examined thus far, the high SO_3 levels subsequently decay, but it can be seen that the flame-gas quench rates can be important for SO_3 formation. If the quench is too fast (e.g., by flames impinging on refractory, or poor mixing in the combustion chamber), the high SO_3 levels can be "frozen" into the flue gases, whereas a slow quench favors reduction to the low equilibrium values at high temperatures..

One other flame mechanism has been noted by Levy and Merryman (618). In probing H_2S-O_2-Ar (or N_2) flames, they noted a small level of SO_3 in the early part

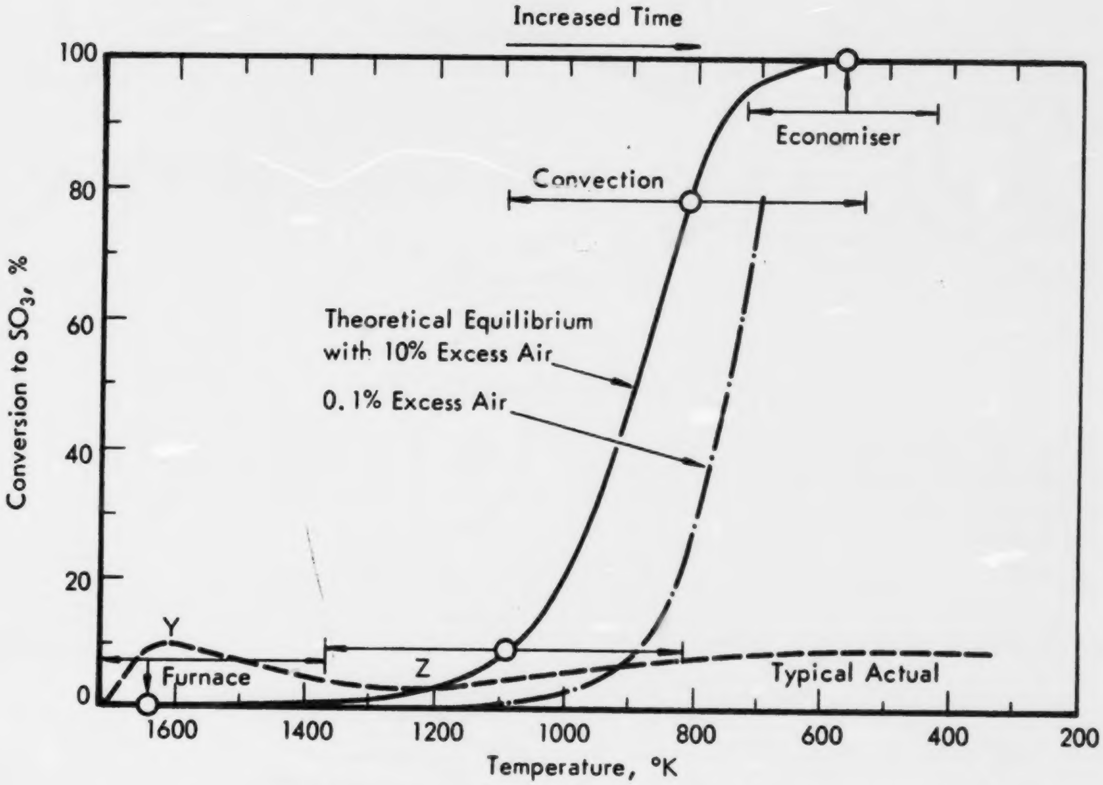


Figure 9. THE VARIATION OF THE THEORETICAL EQUILIBRIUM YIELD AND POSSIBLE ACTUAL YIELD OF SO_3 WITH TIME IN A BOILER

of the flame which subsequently disappeared. This was attributed to the reaction

$$SO + O_2 + M \longrightarrow SO_3 + M \qquad (38)$$

Since this occurs early in the flame where there are still plenty of reducing radicals around, the SO_3 is quickly removed. Hence, this mechanism probably does not contribute much to the final level of SO_3 emitted from the flame. This conclusion appears to be corroborated by experiments in which SO_2 added just at the tip of the flame produced the same SO_3 levels as when the SO_2 was added with the fuel (345).

The level of SO_3 emitted from a flame increases with the sulfur level of the fuel (see Figures 10 and 11). However, the percentage of total sulfur appearing as SO_3 decreases as the sulfur level of the fuel increases (345), (615), (619), (620). The reason for this is not completely understood, but it is known that sulfur in flames can be very effective in breaking reaction chains. Halstead and Jenkins (639) observed the decay of H and OH in H_2-O_2-N_2 flames doped with SO_2. They found that the free radicals disappeared faster when SO_2 was present and interpreted this in terms of the mechanism

$$H + SO_2 + M \rightleftarrows HSO_2 + M \qquad (39)$$

$$H + HSO_2 \longrightarrow SO_2 + H_2 \qquad (40)$$

$$OH + HSO_2 \longrightarrow SO_2 + H_2O \qquad (41)$$

yielding

$$k_{39}k_{40} = 8.2 \pm 0.8 \times 10^{-30} \text{ cm}^6/\text{molecules}^2/\text{sec}$$

$$k_{39}k_{41} = 1.3 \pm 0.3 \times 10^{-30} \text{ cm}^6/\text{molecules}^2/\text{sec}$$

at 2000°K. Reactions 39 to 41 coupled with the free-radical generating reactions in the flame might lead to a reduction of atomic oxygen level in the flame as sulfur level increases. Durie et al (727) confirmed these values for k_{40} and k_{41}.

The main variable determining the SO_3 level emitted from the flame appeers to be the level of excess air used in combustion. Several studies (345), (614), (615), (621), (622) have shown that the level of SO_3 is very sensitive to excess air, especially in the region below 10% excess air (see Figures 12 and 13). Hedley (614) even argues that there is a critical excess air range for SO_3 formation near 30-40%. For high excess air levels it can be argued that the increase in available oxygen is more than offset by the reduction in flame temperature, lowering the atomic oxygen available for reaction 35. The effects of excess air and fuel sulfur level were also examined by Wendt (623) et al (see Figure 14) in a laboratory flat flame. (For the purposes of modeling these data, the complete set of conditions and the temperature profile are shown in Table 7 and Figure 15.)

The other variable of importance is the flame temperature. It would seem that high flame temperatures might increase the atomic oxygen levels and, hence, increase formation of SO_3. This effect has been observed by Crumley and Fletcher (619). They measured the SO_3 produced by a CS_2-doped kerosine flame while varying the flame temperature by heating the secondary air fed to the

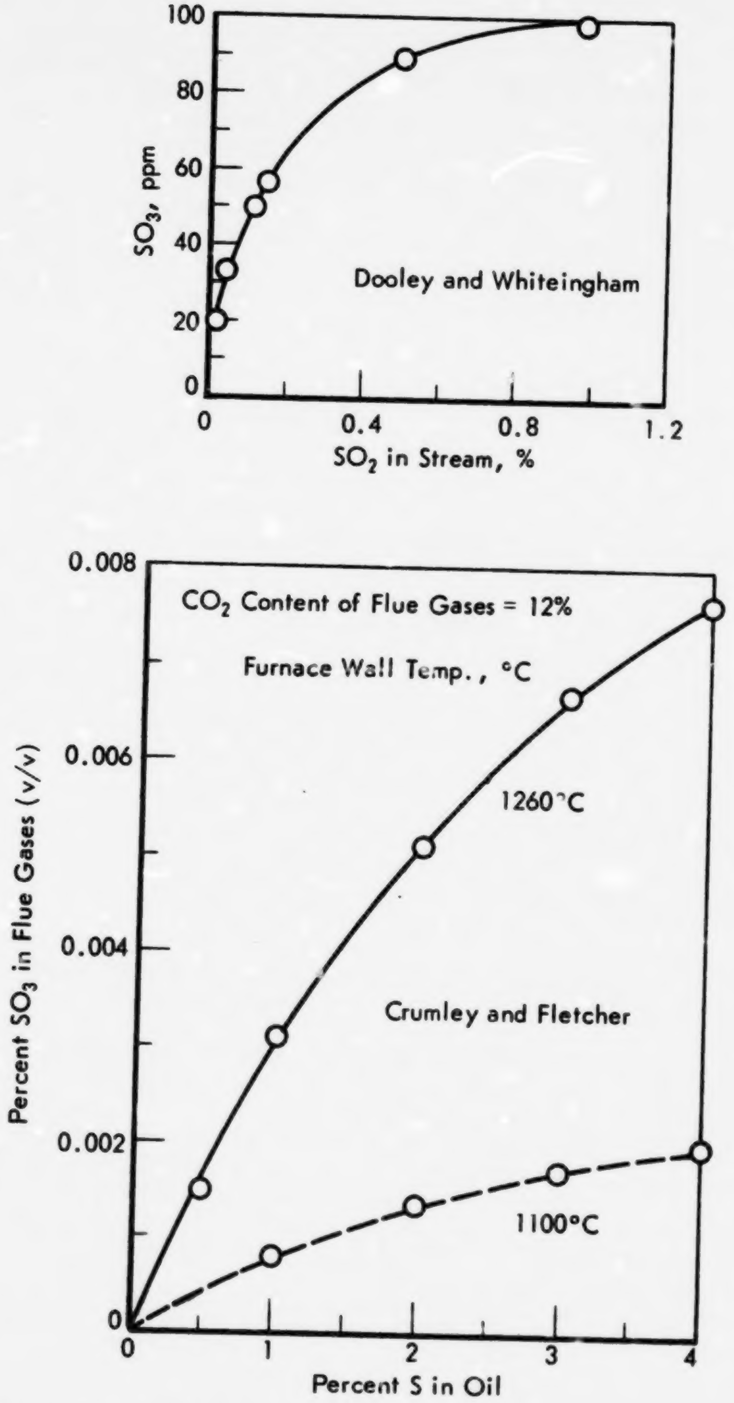
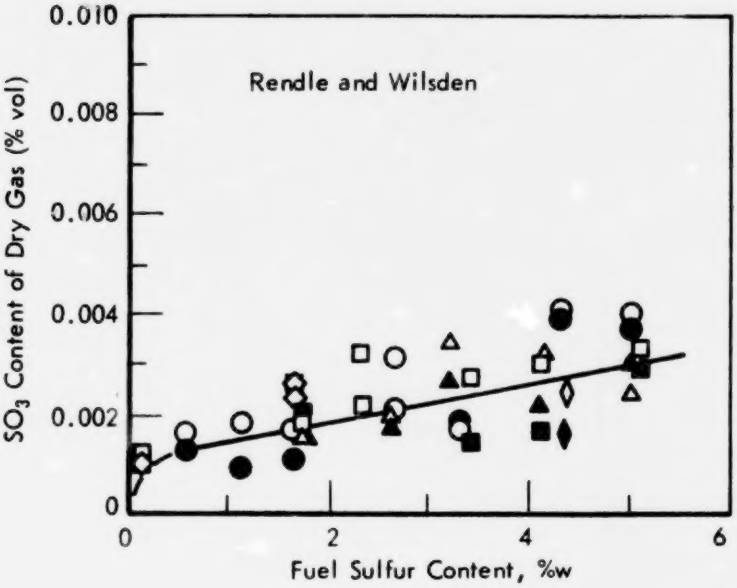


Figure 10. EFFECT OF FUEL SULFUR LEVEL ON SO_3 FORMATION



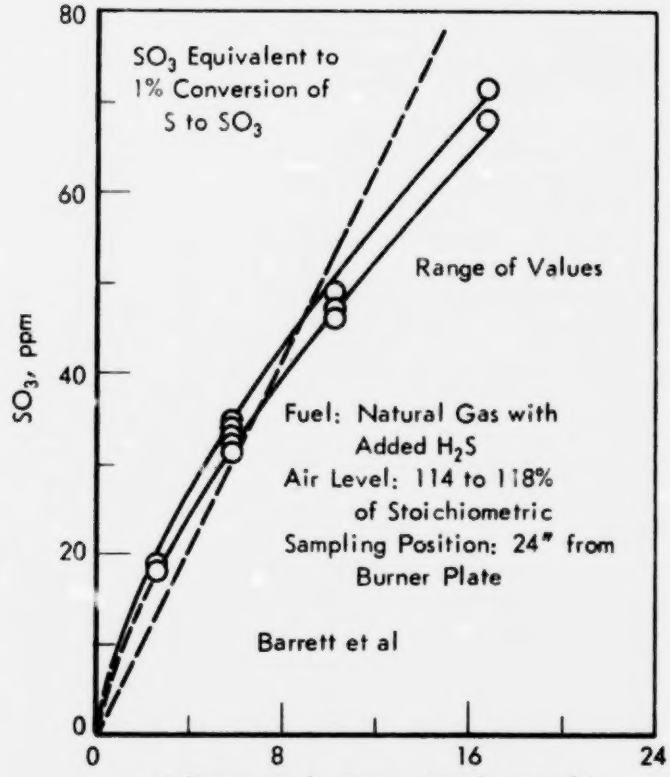


Figure 11. EFFECT OF FUEL SULFUR LEVEL ON SO$_3$ FORMATION

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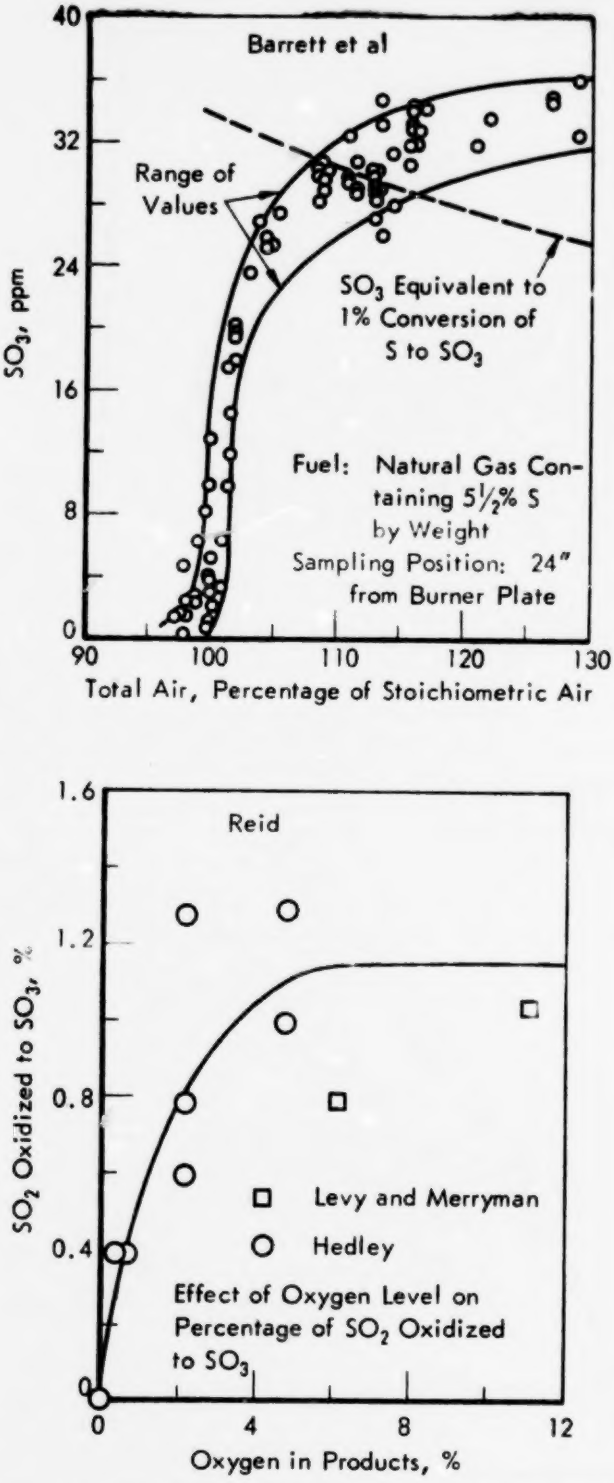


Figure 12. EFFECT OF EXCESS AIR ON SO_3 FORMATION

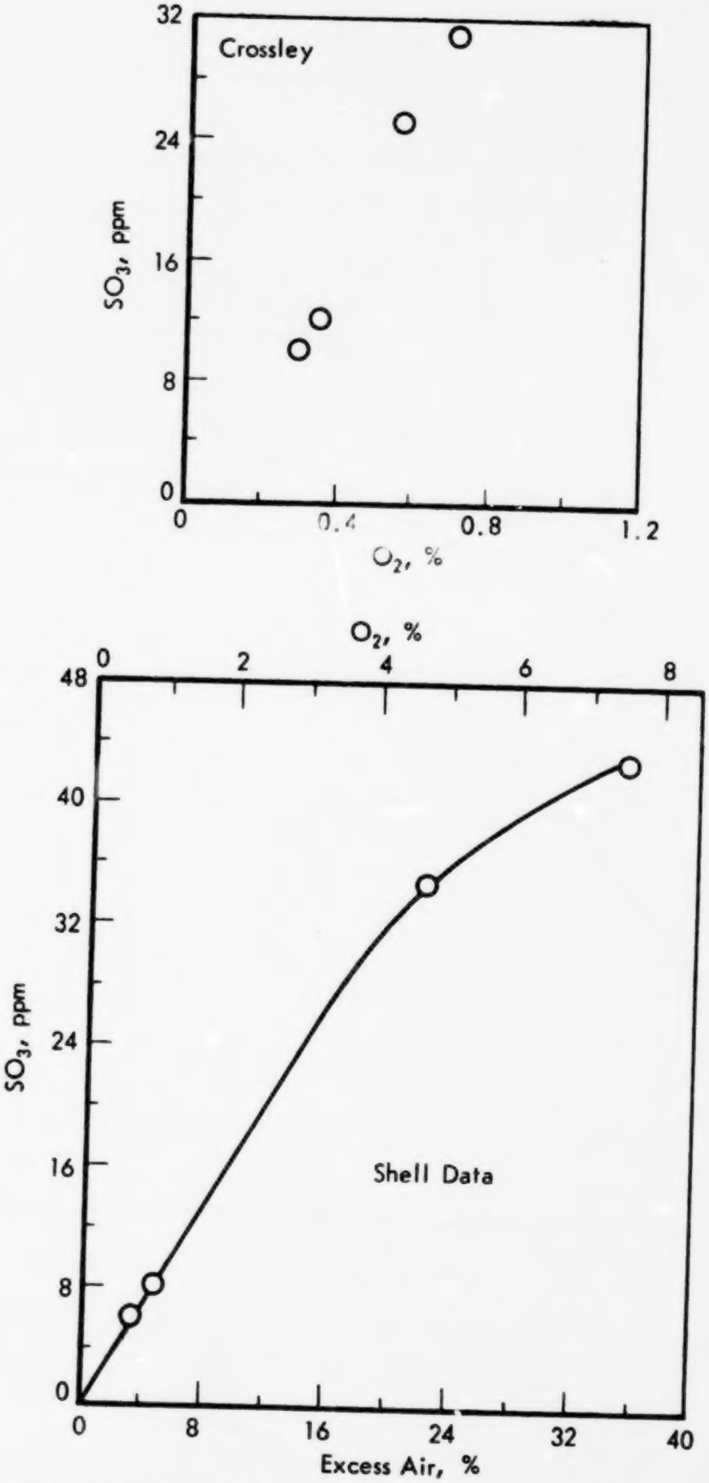


Figure 13. EFFECT OF EXCESS AIR ON SO$_3$ FORMATION

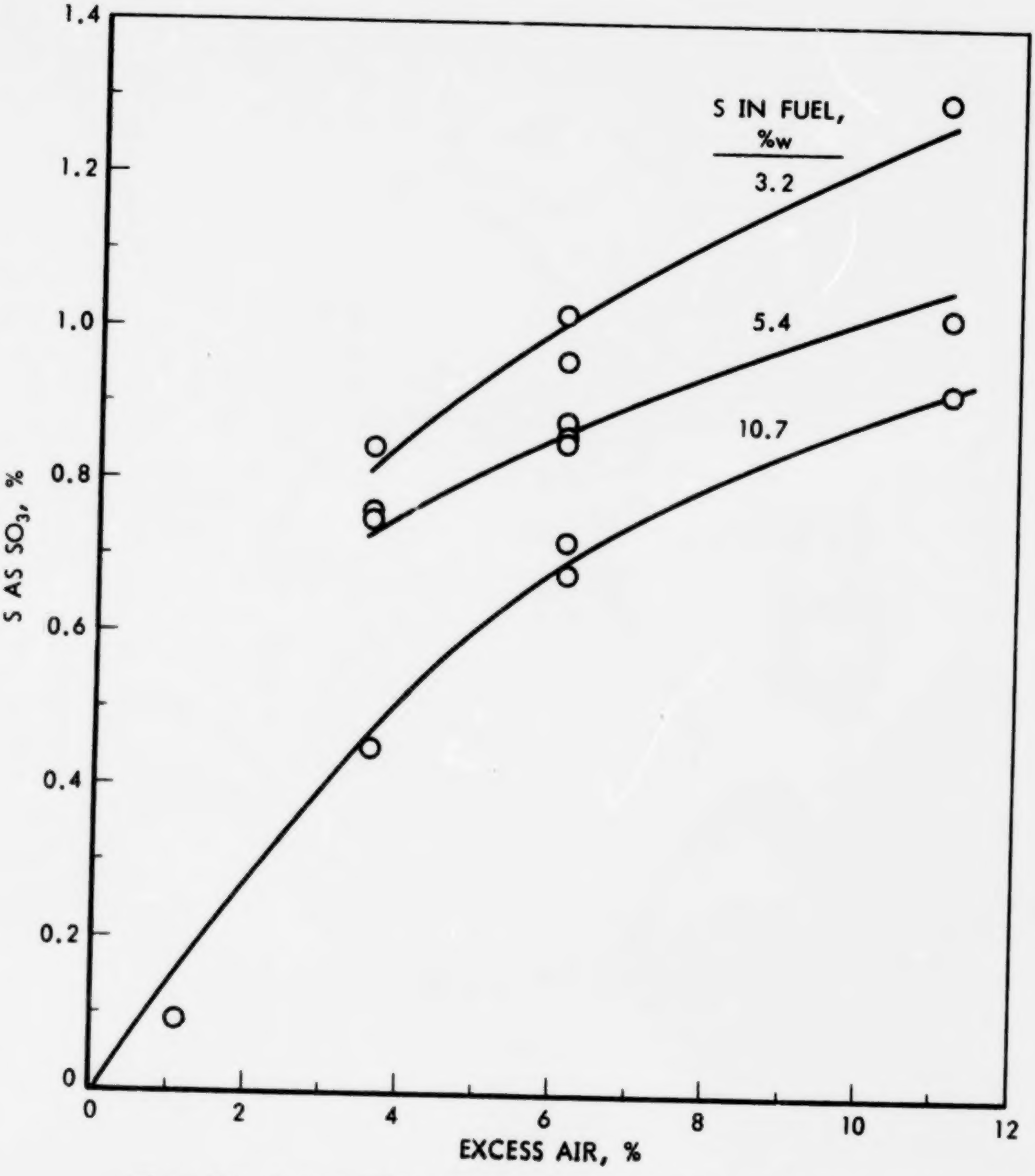


Figure 14. FLAME FORMATION OF SO_3 AS FUNCTION OF EXCESS AIR AND SULFUR LEVEL OF FUEL

Table 7. EXPERIMENTAL DATA ON SO_3 FORMATION

Wendt et al (623)

Run No.	CH_4 Rate scc/min	SO_2 Rate		Air Rate		Height of Probe Above Burner cm	SO_2 Sample mg $SO_4^=$	SO_3 Sample mg $SO_4^=$	% S as SO_3
		scc/min	%w S in Fuel	scc/min	% Excess Air				
LR-10667-18	1475	100	10.7	14200	1.1	1.2	224.7	.2	.09
-40	1475	45	5.4	14900	6.1	1.2	93.3	.8	.85
-45	1475	100	10.7	15600	11.1	1.2	186.6	1.73	.92
-46	1475	100	10.7	14900	6.1	1.2	203.4	1.40	.68
-50	1475	45	5.4	15600	11.1	1.2	88.1	.91	1.02
-51	1475	45	5.4	14900	6.1	1.2	91.0	.79	.86
-52	1475	45	5.4	14550	3.6	1.2	91.0	.65	.71
-53	1475	100	10.7	14900	6.1	1.2	202.3	1.46	.72
-54	1475	45	5.4	14900	6.1	1.2	93.3	.83	.88
-56	1475	100	10.7	14550	3.6	1.2	213.1	.97	.45
-57	1475	25	3.2	15600	11.1	1.2	50.01	.64	1.27
-58	1475	25	3.2	14900	6.1	1.2	54.84	.53	.96
-59	1475	25	3.2	14550	3.6	1.2	55.56	.47	.84
-60	1475	25	3.2	14900	6.1	1.2	53.16	.55	1.02
-61	1475	45	5.4	14500	3.6	2.0	95.22	.72	.75

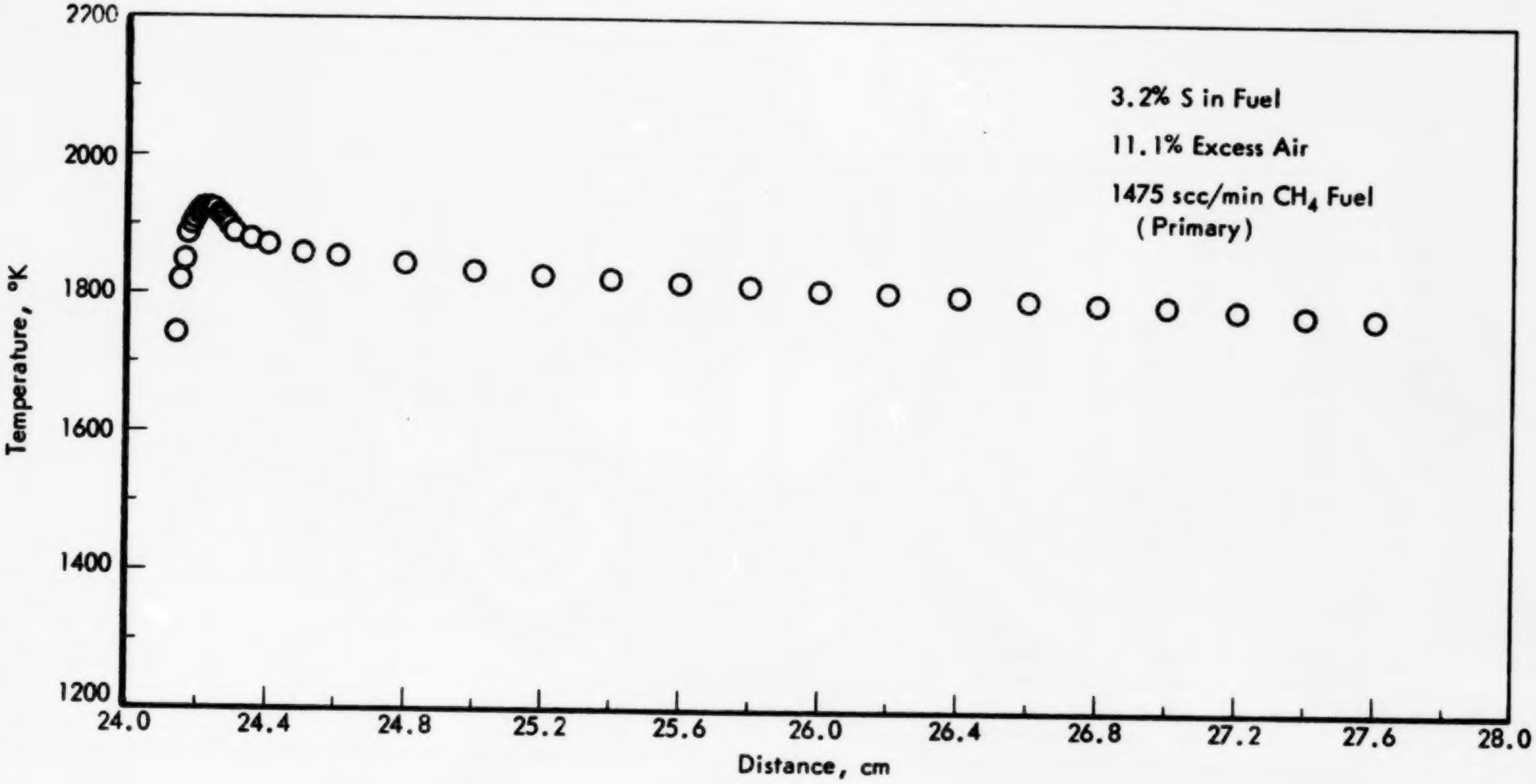


Figure 15. TYPICAL TEMPERATURE PROFILE - INJECTOR NOT IN POSITION

burner. The result was that SO_3 measured just beyond the flame increased up to a temperature of 1750°C and then leveled off (see Figure 16). Levy and Merryman (616) report the opposite effect. However, they were comparing two different flames, H_2S-O_2-Ar and $H_2S-O_2-N_2$; hence, the lower level of SO_3 in the flame with the highest temperature ($H_2S-O_2-N_2$) may be attributable to other mechanisms.

The overall conclusion was that SO_3 can be formed in flames and the excess air, flame quench rate, and flame peak temperature can have significant effects. In a variety of combustion rigs, from bunsen burners to small domestic boilers, the flame produced SO_3 has been found to be about 1-3% of the total sulfur in the fuel.

In the high-temperature gaseous region outside the flame, the SO_3 level can decrease or increase depending on which of two mechanisms dominates. If the quench rate is not too fast, the super-equilibrium flame-produced SO_3 levels can decay. Alternatively, SO_2 can be oxidized to increase the level of SO_3.

As mentioned above, evidence (614), (616) does exist for the formation of super-equilibrium ($SO_2 + 1/2\ O_2 = SO_3$) amounts of SO_3 in flames. Maximum values of 15-20 ppm SO_3 have been observed. The results of Hedley (614) indicate that the maximum SO_3 level occurs within about 30 msec, and the decay to equilibrium is achieved somewhere around 0.2 sec. Since the experimental rigs are smaller than industrial furnaces, it was concluded that flame-produced SO_3 would probably not significantly affect the SO_3 levels in industrial flue gases. However, this conclusion can easily be incorrect if furnace mixing and flame patterns interact to yield a quick quench.

There are two possible mechanisms for the homogeneous oxidation of SO_2 in this region. The first is by direct thermal reaction with O_2, and the second involves a catalytic cycle with the nitrogen oxides.

Available evidence indicates that the thermal oxidation

$$SO_2 + 1/2\ O_2 = SO_3 \qquad (42)$$

proceeds at a very slow rate. Cullis, et al (342), and Ladner and Pankhurst (625) have shown that mixtures of O_2 and SO_2 react at very small rates at about 1000°C. For example, at 950°C, $[SO_2] = [O_2] = 2.6 \times 10^{-3}$ mole/ℓ, the rate of SO_3 formation was found to be $\sim 7 \times 10^{-8}$ mole/ℓ/min in a silica vessel. The rate was shown insensitive to large surface-to-volume ratio changes. In checking the catalytic activity of various materials, Barrett et al (615) passed mixtures of air and 0.7% SO_2 through a quartz tube. There was no direct data for 42, but the reaction appeared to be extremely slow. Using the data of Cullis et al (342), a value of

$$k_{42f} \sim .063\ \ell^{\frac{1}{2}}/\text{moles}^{\frac{1}{2}}/\text{min}$$

at 950°C is obtained. Assuming a flue gas contains 1000 ppm SO_2 and 2% O_2, this yields an SO_3 formation rate of ~ .02 ppm/sec.

This oxidation of SO_2 by a catalytic cycle involving nitrogen oxides appears to be a possible significant contributor to SO_3 levels of the flue gas. D. H. Morman of these laboratories, in testing analytical methods for the determination of SO_3 in combustion gases, found that additions of 100 ppm NO_2 to a

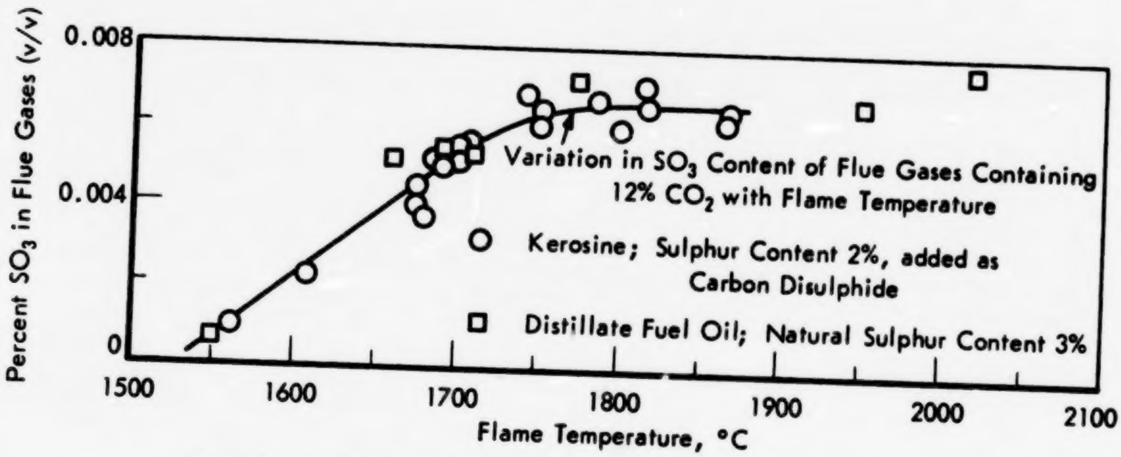


Figure 16. EFFECT OF FLAME TEMPERATURE ON SO_3 FORMATION

Crumley and Fletcher

500 ppm SO_2 stream with a residence time of about 3 sec at 300-400°C resulted in an increase of 5 ppm SO_3 over that obtained with no NO_2 added. NO additions were found to have no effect up to 300 ppm. Shaw and Green (337) found that when NO (600-900 ppm) plus CO (250-1000 ppm) were simultaneously added to gases with 2000 ppm SO_2 at ~1000°C, 70-100 ppm SO_3 resulted after about 1.5 sec. NO additions by themselves produce no measurable SO_3. Cullis et al (392), working with high levels of SO_2 and O_2 ($\sim 10^{-3}$ moles/ℓ) found that additions of NO of the order of 10^{-3} mole/ℓ increased the rate of formation of SO_3 by two orders of magnitude.

The basic mechanism for this oxidation is thought to be

$$SO_2 + NO_2 \longrightarrow SO_3 + NO \qquad (43)$$

with the NO_2 being formed by

$$NO + O \longrightarrow NO_2 \qquad (44)$$

or by

$$NO + NO + O_2 \longrightarrow NO_2 + NO_2 \qquad (45)$$

The chain-branching oxidation of CO in the work of Shaw and Green is presumably the source of atomic oxygen. Armitage and Cullis (626) obtained a value of $k_{43} = 10^{12.8} \exp(-27000/RT)$ cm^3/mole/sec for reaction 43. This activation energy is in excellent agreement with that obtained by Boreskov and Illarionov who find 26500 kcal and show reaction 43 to be extremely rapid. Hence, in furnaces where the high temperatures preclude high levels of NO_2, the rate may depend on the oxidation of NO. Indeed, Cullis et al (342) found the rate of SO_3 formation for high SO_2 levels to be given by the rate of oxidation of NO.

Hence, it appears that this mechanism can be a significant source of SO_3. At present, furnaces usually produce about 300-600 ppm NO by the fixation of atmospheric nitrogen in the flame. High peak temperatures and longer residence times at high temperatures favor NO formation. If one tries to minimize SO_3 formation by designing for a long, high-temperature soak, this may backfire by increasing the NO level and thereby the effect of the above SO_2 oxidation mechanism. On the other hand, if one tries to minimize NO formation by a quick quench of the combustion flame, formation of SO_3 may increase.

Process Modifications to Reduce SO_3 Emissions

The mechanisms of SO_3 formation in process heaters described above suggest several design or operating modifications which might reduce SO_3 emissions. Some have been tried; others have not been tried. In any given case, definition of the specific mechanism leading to the troublesome SO_3 levels would allow selecting the best solution.

Low Excess Air Combustion

Since the oxidation of SO_2 depends on the availability of excess O_2 in the flue gas, reduction of the O_2 level should inhibit SO_3 formation by all the mechanisms described above. This has indeed been observed in practice on small burners as well as large furnaces. Figure 12 shows the effectiveness of O_2 reduction on the

SO_3 levels from flames; the SO_3 level is particularly sensitive below about 10% excess air.

Several reports attest to the effectiveness of this operating modification on large-scale units. Crossley (621) reports that Britain's Central Electricity Generating Board (C.E.G.B.) has been able to operate oil-fired boilers at 1% O_2 in the flue gas reducing the SO_3 levels from previous values of 30 ppm to about 6 ppm. Crossley also reports that Deutsche Shell have operated at 0.3% O_2 yielding 10 ppm SO_3. Munroe (628) describes the use of 1-5% excess air in oil-fired forced converter furnaces. He claims reduction in SO_3 and nitrogen oxides with clean (soot-free) combustion. Glaubitz (629) also describes redesign of oil burners to burn with 1% excess air.

If care is taken to reduce the excess air in the firebox, the work of Barrett et al (615) indicates that air leakage should be minimized. They found that if air is injected downstream of a stoichiometric flame appreciable increases in SO_3 occur if the gas temperature is still above 2100°F. Of course, any air leakage will also allow catalytic oxidation and oxidation via the NO_x cycle to occur.

Flame Quench

Although there is no conclusive proof that high SO_3 levels have been caused by fast quench of the flame reactions, the possibility still exists. Hence, it is worthwhile to ensure that extreme quench rates are not obtained. Attention is directed to the effect of primary and secondary air injection and to the mixing and flame patterns within the furnace. High SO_3 levels may be another undesirable effect of flames impinging upon refractory.

Staged Combustion

Two-Stage Air Addition

Two-stage air addition can minimize the emission of SO_3 from the flame region. The major part of the combustion occurs in the flame with a stoichiometric or sub-stoichiometric atmosphere. The rest of the air needed to complete combustion is added beyond the flame. Since the oxidizing atmosphere occurs in a region of lower temperature and lower level of combustion, SO_3 formation should be minimized.

Reports concerning the effectiveness of this modification conflict. Austin and Chadwick (630) report no effect on the SO_3 level, whereas Coykendall (631) reports reductions in SO_3 level. Both of the above reports indicate substantial reductions in NO_x levels, and it has been reported that NO_x levels were substantially reduced (from 1400 ppm to 250 ppm) at PG&E's Moss Landing power plant by this technique. In view of the work of Barrett et al (615), who found that significant increases in SO_3 occurred if air was added to flue gases above 2100°F, the precise point of injection of the secondary air is important in determining the SO_3 emission reduction achieved by this technique.

Two-Stage Fuel Addition or Reburning

Two-stage air addition minimizes SO_3 formation in combustion, whereas two-stage fuel addition would reduce the SO_3 formed. This could be applied in situations where it is not possible to burn with sufficiently low excess air to minimize formation. The idea is to add a clean (sulfur free) secondary fuel to the gases beyond the flame in sufficient quantities to reduce the resultant flue gas to 0% O_2. This should then cause reduction of the SO_3 emitted from the primary flame.

Recent experiments (623) by Shell indicate that injection of methane and CO above the flame of a small flat-flame burner in sufficient quantities to reduce all excess O_2 substantially reduces the SO_3 level.

This idea also forms the basis of U.S. patent No. 3463599 assigned to Esso.

The only other report found regarding this technique was a reference (632) to an attempt by the British C.E.G.B. to reduce SO_3 levels by injection of CO into the flue gases. Injection took place at a point where the flue gas temperatures were 900°F. It is reported that additions of ten times the stoichiometric amount required to react with all SO_3 present produced no reduction in the SO_3 level. The temperature was probably too low. Perhaps combustion of the added fuel is required. At 900°F, CO would not be expected to burn.

The Use of Additives

The literature regarding the use of additives to control cold end corrosion in furnaces and boilers is extensive. However, the results seem unclear because no one has really performed an exhaustive study of all possible additives under controlled and comparable conditions.

The basic idea behind the use of additives is to inject into the furnace environment a component which can

1. Preferentially react with atomic oxygen in the flame to inhibit SO_2 oxidation.
2. Chemically react with SO_3 to remove it from the gas stream.
3. Physically adsorb SO_3 to remove it from the gas stream.

In some cases, if the additive is fed to the fuel, it can perform more than one of the above functions. Here, we will restrict discussion to atomic oxygen scavengers, since the data may give insight into the role of O atoms in SO_2 oxidation.

Several reports (345), (616), (626) have appeared regarding additions of constituents to the flame to specifically act as oxygen atom scavengers. Compounds found capable of lowering SO_3 levels are ethyl alcohol, benzene, ethyl nitrate, pyridine, carbon tetrachloride, and nitric oxide (345) (in order of increasing effectiveness) and hydrogen (616). Ammonia and steam were also tried (624) but found ineffective.

The experiments quoted above (345) were performed in a Bunsen burner, where the SO_3 levels were measured before the high-temperature oxidation reactions had time to occur. No tests have been reported for NO additions in furnaces. Until this is done, the overall effect of NO additions in resultant SO_3 levels at the stack will be unclear.

Metals in flames can also be good atomic oxygen scavengers. Species found effective (630), (622), (620), (632), (634) as oil-soluble additives, metal oxide suspensions, or metal suspensions have been Mg, Zn, Ca in order of decreasing effectiveness. It should be noted that some problems with furnace deposits resulting from these additions have been reported.

In summary, additives may prove useful, but their application on a large scale has not been demonstrated as problem-free. Indeed, use of gaseous atomic oxygen scavengers has only been tried on laboratory-scale equipment.

Table 8. AVAILABLE DATA ON THE KINETIC CONSTANT OF THE REACTION

$SO_2 + O + M \xrightarrow{k_{35f}} SO_3 + M$

Source	k_f ($cm^6/moles^2/sec$)	Temperature
Jaffe & Klein (635)	1.4×10^{16} (P_T = 2 mm Hg) 0.92×10^{16} (P_T = 1 atm) ($M = SO_2 + NO_2$)	Room temp
Webster & Walsh (636)	1.0×10^{16} ($M = H_2 + O_2$)	784°K
Thrush & Halstead (637)	3.6×10^{16} (M = Ar)	Room temp
Halstead & Thrush (638)	$4.7 \pm 0.8 \times 10^{15}$ (M = Ar)	293°K
Kaufman (361)	3×10^{16} ($M = SO_2$)	Room temp
Mulcahy, Steven & Ward (343)	$2.7 \pm 0.5 \times 10^{15}$ ($M = O_2$) $2.4 \pm 0.15 \times 10^{15}$ (M = Ar) $10 \pm 4 \times 10^{15}$ ($M = SO_2$)	300°K 300°K 300°K
Levy & Merryman (324)	$2.2\text{-}22 \times 10^{15} \exp(-6000/RT)$	
Merryman & Levy (617)	$2.4 \times 10^{17} \exp(-2500/RT)$	average value from literature

Summary of Literature Review

The literature review indicates many areas of ignorance and controversy about the mechanisms by which fuels containing N and S burn and the products resulting from the combustion. Here we merely reiterate those points which we think most merit further study.

1. What are the rates and products of pyrolysis of coal and residual oils and especially how is the nitrogen distributed between the volatile material and the residual char?
2. What reactions govern the combustion of the nitrogen in chars, and what is the ratio of N_2 to NO_x in the products?
3. What reactions govern combustion of cyanides and ammonia, and what are the rates of the elementary steps?

4. How is the N-to-N bond formed in combustion of fuel nitrogen?

5. How is SO_3 formed in furnaces?

6. How does the presence of nitrogen oxides affect the oxidation of SO_2?

7. How does inhibition caused by the presence of SO_2 affect the formation of nitrogen oxides?

8. Can the pollutants SO_3 and NO_x be reduced to less noxious forms by homogeneous gas-phase reactions, and if so, how can this be done practically?

9. By what mechanism is "prompt" NO formed?

10. What reactions besides the Zeldovich pair contribute significantly to fixation of atmospheric nitrogen?

11. Finally, how may the complex physical and chemical process occurring in furnaces be modeled mathematically in a practical fashion?

Results of Modeling Studies

Some of the questions listed in the previous section can be answered, at least partially, through computer-aided modeling of chemical mechanisms. In this section, we report the results for six such studies. Treated are: (1) Prompt NO via cyanide intermediates; (2) Fixation of atmospheric nitrogen; (3) Fate of fuel nitrogen in a gaseous diffusion flame; (4) SO_3 formation by uncatalyzed reactions; (5) Synergistic reactions of SO_x and NO_x; and (6) Reduction of NO by H_2 in a secondary flame (reburning). Each of the studies is described in detail below.

"Prompt" NO by Cyanide Reactions

Fenimore (721) noted that substantial amounts of NO were formed very rapidly in the flame front of methane-air flames but not in CO-air or H_2-air flames. He suggested that reactions such as

$$CH_2 + N_2 = HCN + \cdots \qquad (47)^*$$

$$C_2 + N_2 = CN + CN \qquad (48)$$

might be responsible for the breaking of the $N\equiv N$ bond. Subsequent reactions of HCN and other molecules containing a single nitrogen atom could easily lead to nitrogen oxides. An alternative suggestion for the formation of "prompt" NO is that the chain-branching reactions involved in fuel combustion generate super-equilibrium concentrations of free radicals, especially O atoms, which then react rapidly with N_2. This explanation, treated in more detail in the next section, cannot explain the observation of Fenimore that CH_4 flames made much prompt NO while CO and H_2 flames did not.

To test the Fenimore conjecture quantitatively, we have set up a model for methane combustion involving, in addition to generally accepted reactions, the following

$$CH_3 + OH = CH_2 + H_2O \qquad \text{PROM 1} \qquad (49)$$

$$CH_3 + N_2 = HCN + NH_2 \qquad \text{PROM 3} \qquad (50)$$

$$CH_2 + N_2 = HCN + NH \qquad \text{PROM 2} \qquad (51)$$

$$CH_2 + O_2 = HCO + OH \qquad \text{PROM 4} \qquad (52)$$

With the intention of finding a maximum possible rate of N_2 fixation by the cyanide route, we have taken maximum conceivable rates (steric factor of unity) for reactions PROM 1, PROM 2, and PROM 3 and a rather low rate for PROM 4. Table 9 shows the complete set of reactions considered, and Table 10 gives the reaction rates used for those reactions not included in our library of Arrhenius parameters (Appendix I).

(*) **Equation 46 intentionally omitted.**

Table 9. REACTIONS INCLUDED IN THE CYANIDE ROUTE TO PROMPT NO

1.	SBOW 1	$CH_4 + M + = CH_3 + H + M$
2.	SBOW 2	$CH_4 + O_2 + = CH_3 + HO_2$
3.	SBOW 3	$O_2 + M + = O + O + M$
4.	SBOW 4	$CH_4 + O + = CH_3 + OH$
5.	SBOW 5	$CH_4 + H + = CH_3 + H_2$
6.	SBOW 6	$CH_4 + OH + = CH_3 + H_2O$
7.	SBOW 7	$CH_3 + O + = HCHO + H$
8.	SBOW 8	$CH_3 + O_2 + = HCHO + OH$
9.	SBOW 9	$HCHO + OH + = CHO + H_2O$
10.	SBOW 10	$CHO + OH + = CO + H_2O$
11.	SBOW 11	$CO + OH + = CO_2 + H$
12.	SBOW 12	$H + O_2 + = O + OH$
13.	SBOW 13	$O + H_2 + = H + OH$
14.	SBOW 14	$O + H_2O + = OH + OH$
15.	SBOW 15	$H + H_2O + = H_2 + OH$
16.	SBOW 16	$H + OH + M = H_2O + M$
17.	SBOW 18	$CHO + M + = H + CO + M$
18.	PROM 1	$CH_3 + OH + = CH_2 + H_2O$
19.	PROM 2	$CH_2 + N_2 + = HCN + NH$
20.	PROM 3	$CH_3 + N_2 + = HCN + NH_2$
21.	PROM 4	$CH_2 + O_2 + = HCO + OH$

Table 10. ARRHENIUS PARAMETERS USED IN STUDY OF PROMPT NO VIA CYANIDES

Reaction		Rate Expressions, cm^3, sec, g mole	
		Forward	Reverse
PROM 1	$CH_3 + OH = CH_2 + H_2O$	$.771 \times 10^{15} \exp(-4180/RT)$	$.296 \times 10^{16} \exp(-9210/RT)$
PROM 2	$CH_3 + N_2 = HCN + NH_2$	$.46 \times 10^{16} \exp(-19000/RT)$	$.605 \times 10^{15} \exp(-2610/RT)$
PROM 3	$CH_2 + N_2 = HCN + NH$	$.204 \times 10^{16} \exp(-41700/RT)$	$.734 \times 10^{15} \exp(-1950/RT)$
PROM 4	$CH_2 + O_2 = HCO + OH$	$.738 \times 10^{15} \exp(-1700/RT)$	$.678 \times 10^{14} \exp(-90900/RT)$

The initial calculations were for a plug flow reactor, isothermal at 2100°K, burning methane at 114.2% of theoretical air. This corresponds to a feed composition:

Species	Mole Fraction
CH_4	.08402
O_2	.1919
N_2	.7241

Large quantities of HCN, NH, and NH_2 were produced indicating that Fenimore's mechanism can be significant if the rates of reactions PROM 1 to 3 are large enough and the rate of reaction PROM 4 is low enough. Further work appears justified to find a set of rates consistent with the yields of prompt NO found by Fenimore and by others [especially Lange (544)]. Such a model, however, will remain conjectural until a firmer base is found for estimating the rates of reactions PROM 1 to PROM 4 and of other rates which might be important.

Some results from the run described above are:

Residence time, sec	0	10^{-5}	10^{-3}
Mole Fractions			
CH_4	.084	.039	10^{-10}
CH_3	0	.0014	10^{-10}
CH_2	0	10^{-5}	10^{-11}
OH	0	.0022	.008
HCN (in ppm)	0	1120	1.0
NH (in ppm)	0	940	1.0
NH_2 (in ppm)	0	200	0.01

Hence, it appears that the compounds with one nitrogen atom appear at the 1000 ppm level in periods of 10 microseconds and then decay back to equilibrium. Remember that in this calculation no means was provided for oxidation of HCN, NH_2, and NH. In a real flame, such oxidation would be expected to convert an appreciable fraction (say, one-half) of these compounds to NO.

Of the two reactions

$$CH_3 + N_2 = HCN + NH_2 \tag{53}$$

$$CH_2 + N_2 = HCN + NH \tag{54}$$

the latter is the more important according to this model.

Fixation of Atmospheric Nitrogen

Basic to any model for the prediction of the NO_x content of the gases produced by a combustion process is the mechanism by which the nitrogen in the atmosphere is converted into NO_x. Since the time of Zeldovich (542), it has been known that the most important reactions, at least for normal combustion, are

$$N_2 + O = NO + N \tag{55}$$

$$N + O_2 = NO + O \tag{56}$$

It is possible, however, that reactions other than these are sometimes important. Moreover, the rate constants for 55 and 56 are not known exactly, and there exists some controversy about how the concentration of oxygen atoms is to be calculated. We investigated these points by comparing computer-generated solutions for several mechanisms with the data of Lange (544). Since it is the most complete published to date, the model proposed by Lange was taken as a point of departure.

The successive computer runs were designed to each answer a specific question.

1. With regard to both N≡N bond rupture and NO bond formation, which reactions in the scheme of Lange are significant?
2. Do the additional reactions suggested by Wilde (733) contribute to NO_x make?
3. What error results from shortening the set of 21 reactions of Lange to only those found significant on the one hand and to the Zeldovich reactions on the other hand?
4. Can prompt NO be predicted by eliminating the assumption of equilibrated radicals and considering the nitrogen fixation simultaneously with methane combustion?
5. What is the best set of reactions and rate constants for prediction of fixation?

The results of the runs can best be described in reference to Table 11 which shows the reaction scheme used, the physical conditions, and the answers obtained for each run. Additional details are discussed below.

In run Lange 2, we added to the 25 reactions of Lange (544) the two additional reactions suggested by Wilde (773).

$$HNO + NO = N_2O + OH \tag{57}$$

$$HNO + HNO = N_2O + H_2O \tag{58}$$

The assumption of equilibrium radical concentrations was met by introducing artificially large rate constants for reactions

$$O_2 = O + O \tag{59}$$

$$H_2O = OH + H \tag{60}$$

$$H + O_2 = HO_2 \tag{61}$$

In program EXHAUS there is no difficulty in accurately calculating the true deviation of these species from their equilibrium values; this approximation was made only to facilitate comparison with Lange's own theoretical results. The computer printout for run Lange 2 gave directly the rates of each reaction at each step of the integration. From these rates, Figures 17 and 18 were worked up. These show what fraction of the NO bonds made, or NN bonds broken, can be attributed to each reaction. For the conditions of this run (114.2% theoretical air and no

Table 11. FIXATION OF ATMOSPHERIC NITROGEN--SYNOPSIS OF COMPUTER RUNS

Run No.	Purpose of Run	Reactions Used	Reaction Conditions	Results	Conclusions
Lange 2	Determine which reactions contribute to NO_x	LANG 1 to LANG 21 WILD 1 - WILD 2 Equilibrium of Radicals	Those of Lange Expt. No. 2 114.2% theo air 110 preheat plug flow specified time-temp history	66 ppm NO_x made in 0.1 sec compared with 300 ppm observed experimentally of which 100 ppm is "prompt"	See Figures 17 and 18. 1. Only reactions LANG 1, LANG 8, LANG 10 contribute significantly to N≡N bond breakage. 2. Only Reactions LANG 1, LANG 7, LANG 14, LANG 9, LANG 3, LANG 8, LANG 5 contribute significantly to N-O bond production.
Lange 3	What fraction of the NO_x made can be accounted for by the Zeldovich mechanism alone	From run Lange 1 delete all N fixation reactions except LANG 1 and LANG 7	Same as Lange 2	54 ppm NO_x made in 0.1 sec	Roughly 80% of the NO_x produced under the conditions of this run can be attributed to reactions LANG 1 and LANG 7.
Lange 4	Establish base NO_x for Zeldovich mechanism alone but for low excess air	Same as Lange 3	102.2% theo air no preheat plug flow specified time-temp history	136 ppm NO_x made (compared to 640 ppm NO_x experimentally found)	
Lange 6	Determine how much other reactions in Lange model contribute to NO_x	Same as Lange 2	Same as Lange 4	138 ppm NO_x	98% of NO_x is accounted for by the Zeldovich Mechanism under these conditions of low excess air (high temperature)
Fris 8 NFIX 4	Test whether prompt NO can be predicted by integrating simultaneously Methane combustion and fixation	See Table 11 Adjusted rates of Lange used for LANG 1, LANG 2, and LANG 9	Same as for run Lange 2 114.2% theo air no preheat adiabatic flame front and plug flow	See Figures 19, 20	By considering the interaction of methane combustion with the nitrogen fixation, prompt NO can be predicted. The ratio of prompt NO to post-flame NO is the same as in the experiments of Lange, but the absolute values of both are low by about 23%.

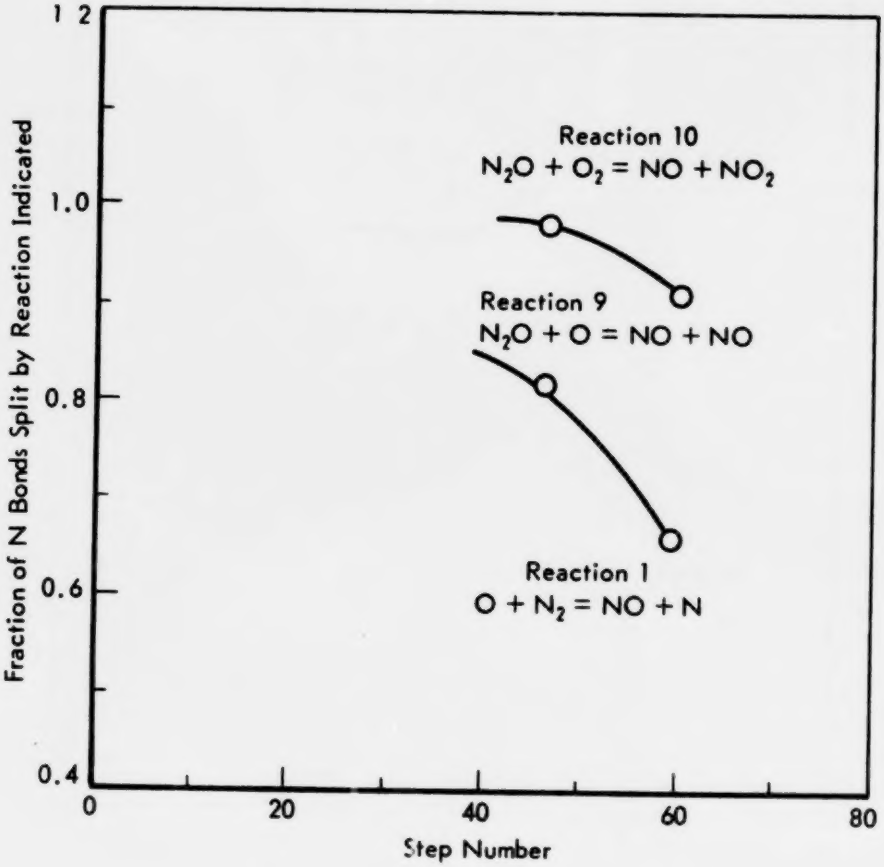


Figure 17. SPLITTING OF N-N BONDS
LANGE RUN 1

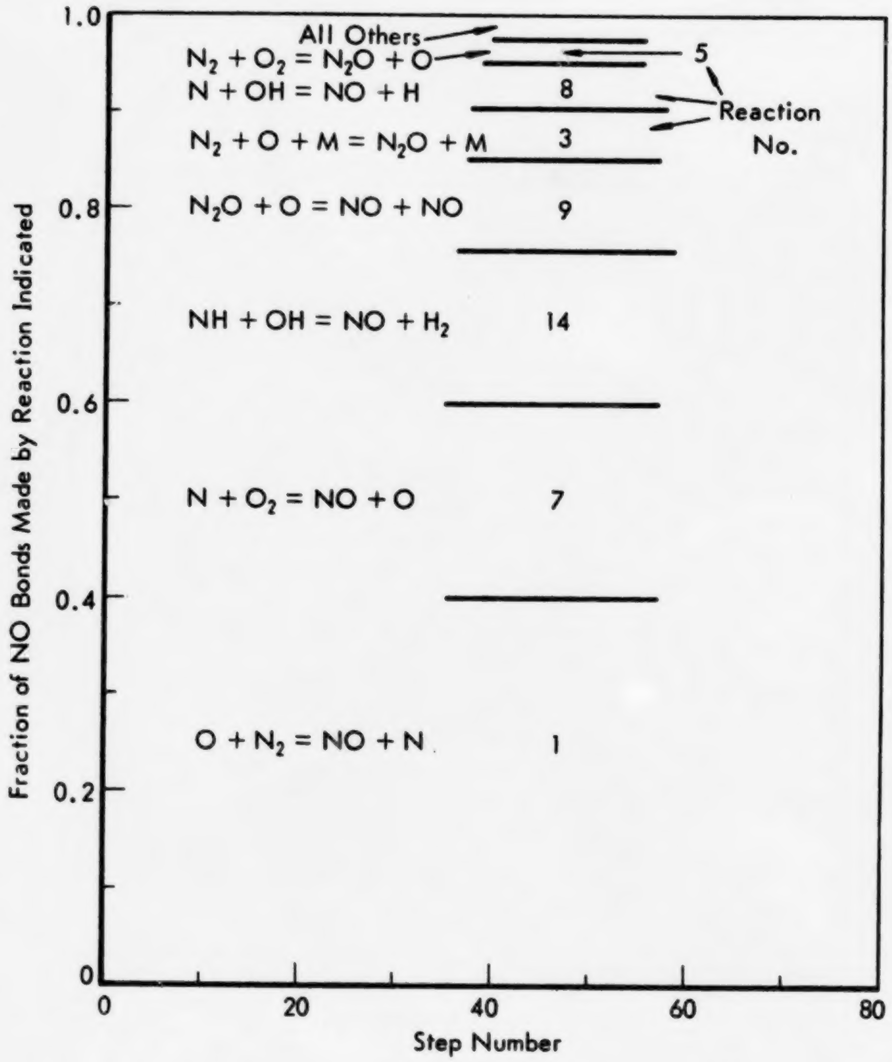


Figure 18. PRODUCTION OF N-O BONDS
LANGE RUN 1

preheat) and for the rates used one can conclude that 13 of the 21 reactions of Lange and both of the reactions of Wilde can be dropped. Of the remaining reactions, the Zeldovich pair LANG 1, LANG 7, account for about 65% of the NN bonds broken and for 60% of the NO bonds made. This conclusion was checked by run Lange 3, similar in all respects to Lange 2, except that only the Zeldovich reactions were retained of all the fixation reactions. Only 22% additional NO_x results from including the other 19 reactions of Lange's mechanism.

A similar comparison was made for a run with low excess air (computer runs Lange 4 and 6). Here, the temperature is higher. Almost all (98%) of the fixation is accounted for by the Zeldovich mechanism.

A large discrepancy between theoretically predicted NO_x and that observed experimentally is displayed by runs Lange 2 to Lange 6, as shown below.

Percent of Theoretical Air	NO_x at 0.1 second Residence Time			
	Experimental		Predicted	
	Prompt	Total	Prompt	Total
114.2	100	300	0	66
102.2	140	640	0	138

Thus, the Lange mechanism, using original rate constants, and assuming equilibrium concentration of free radicals, accounts for none of the prompt NO and for only one-third or less the post-flame NO. Lange met this problem by arbitrarily adjusting the rates for three reactions:

		Adjustment Factor	
LANG 1	$N_2 + O = NO + N$	2.85	(62)
LANG 2	$N_2 + HO_2 = NO + HNO$	0.274	(63)
LANG 9	$N_2O + O = NO + NO$	4.95	(64)

The adjustment to reaction LANG 1 is not unreasonable. The rates recommended by Baulch et al (786) are only 30% lower than the adjusted value of Lange and hence lie well within the range of uncertainty given by Baulch. The adjustments to LANG 2 and LANG 9 seem to have no justification other than the good agreement thereby produced between model and experiment. These values cannot now be recommended for general use; obviously, more data are urgently required.

A further series of runs were made on nitrogen fixation to determine how the methane combustion interacts with the fixation reactions. The intent was to calculate as accurately as is now practicable the entire course of the combustion including the heat balance and the effects of diffusion in the flame front.

The calculations were made at the conditions of Lange's experiment No. 2 and were made with heat balance assuming that heat is lost by radiation at the rate 0.942×10^{-14}cal/sec cm^3K^4, a value which closely predicts the measured temperature profile of Lange. Some explanation of the method of calculation is in order. First, we selected a mechanism for methane combustion which would reproduce approximately the following types of data: (1) ignition delay data in shock tubes, as measured by, for example, Seery and Bowman (526); (2) free radical and formaldehyde concentrations as measured by Fristrom (787); and (3) reaction rates in a Longwell reactor as measured by Morgan (788). The reaction scheme used is shown in Table 11a. It does agree fairly well with data of the types mentioned (e.g., O atom concentrations within a factor of 2 of Fristrom's values). A detailed comparison is outside of the scope of this project; and in fact, the subsequent calculations show that a very accurate methane burning model is not required. The methane has been consumed almost completely before nitrogen fixation starts. Second, we simulated the flame front by a "point-wise" calculation at the flame section where the methane conversion is 90%. The method of doing this is explained in Appendix III. A calculation like this is needed to produce flame ignition, when the feed temperature is low. Third, we continued the calculation as for a heat balanced plug flow reactor using the output temperature and composition for the point-wise calculation. As mentioned above, a radiation heat loss was incorporated to properly predict the experimental temperature. We noted that the combustion of CH_4, CH_3, HCHO, and CHO was substantially completed in a very short time, approximately 200 microseconds, and in this time almost no nitrogen is fixed, and negligible heat is lost. In fact, the fixation process can be predicted by considering only the CO combustion provided that the initial conditions properly reflect the "debris" left by the combustion of methane (and the short-lived intermediates, CH_3, HCHO, and CHO). The calculated debris for the conditions of this run is shown in Table 12. In most of our subsequent runs, we started with this composition and temperature.

Predicted temperature is compared with Lange's measurements in Figure 19, showing the good agreement attained with the heat loss rate selected. A very important point revealed by the calculations was that the temperature is fairly low during the period when prompt NO is being made because the large concentrations of free radicals absorb much heat on dissociation.

Figure 20 shows predicted and experimental NO profiles. In making these calculations, only the Zeldovich fixation reactions and the reactions LANG 3, LANG 4, LANG 5, LANG 6, LANG 8, LANG 9, and LANG 10 involving N_2O were used. The adjusted rate constants of Lange were used. If the original rate constants tabulated by Lange had been used, the predicted NO would have been much lower but the functional relation with time would have been similarly shaped.

This calculation shows that the formation of prompt NO can be predicted by considering the combustion concurrently with fixation. Because of the low temperature prevailing during the formation of prompt NO, the reactions involving N_2O are relatively important compared to the Zeldovich reactions, especially if we accept Lange's large adjustment to the rate of reaction, LANG 9.

NO_x Reduction by Secondary Fuel Injection or Reburning

Much has been published on mechanisms of formation of NO in flames. Very little has been published on reduction of NO in flames. An understanding of NO reduction mechanisms is important for a number of reasons. First, reburning of NO to N_2 may be a useful NO control method for emissions from coal-fired combustion units, where the primary coal flame must be operated at excess air in order to maintain flame stability and prevent formation of soot. Second, in the combustion of oil droplets and coal particles it appears that much of the chemically bound nitrogen remains in the char, which is then consumed by a surface reaction with O_2 molecules to produce CO. A surface reaction with atoms in the char might similarly

Table 11a. REACTIONS USED FOR COMBINED METHANE-BURNING AND NITROGEN FIXATION

Computer Runs FRIS-8, NFIX-4

SBOW 1	$CH_4 + M = CH_3 + H + M$
SBOW 2	$CH_4 + O_2 = CH_3 + HO_2$
SBOW 4	$CH_4 + O = CH_3 + OH$
SBOW 5	$CH_4 + H = CH_3 + H_2$
SBOW 6	$CH_4 + OH = CH_3 + H_2O$
SBOW 7	$CH_3 + O = HCHO + H$
SBOW 8	$CH_3 + O_2 = HCHO + OH$
SBOW 9	$HCHO + OH = CHO + H_2O$
SBOW 10	$CHO + OH = CO + H_2O$
LDSA 1	$CO + OH = CO_2 + H$
SBOW 18	$CHO + M = H + CO + M$
BROK 18	$H_2 + M = H + H + M$
JOHN 11	$O_2 + M = O + O + M$
HOMER 1	$H + OH + H_2O = H_2O + H_2O$
HOMER 2	$H + OH + M = H_2O + M$
BROK 4A	$H + O_2 + H_2O = HO_2 + H_2O$
BROK 4B	$H + O_2 + M = HO_2 + M$
LDSB 1	$H_2 + O = H + OH$
LDSB 3	$H_2 + OH = H_2O + H$
LDSB 5	$H_2O + O = OH + OH$
LDSC 1	$O_2 + H = O + OH$
BROK 6	$H + HO_2 = OH + OH$
THORN 1	$HO_2 + OH = O_2 + H_2O$
BROK 8	$O + HO_2 = OH + O_2$
BROK 10	$H + HO_2 = H_2 + O_2$
	$N + N + M = N_2 + M$
LDSD 3	$O_2 + N = NO + O$
LANG 1 Adj	$N_2 + O = NO + N$
LANG 3	$N_2 + O + M = N_2O + M$
LANG 4	$N_2 + OH = N_2O + H$
LANG 5	$N_2 + O_2 = N_2O + O$
LANG 6	$N_2 + NO_2 = N_2O + NO$
LANG 8	$N + OH = NO + H$
LANG 9 Adj	$N_2O + O = NO + NO$
LANG 10	$N_2O + O_2 = NO + NO_2$

Table 12. "DEBRIS" FROM THE COMBUSTION OF METHANE WITH AIR IN A PREMIXED FLAME

Conditions of Calculation

114.2% of theoretical air (dry)
298°K feed temperature
200 μs residence time in flame front and post-flame region required to destroy 99.99+% of methane
1770°K debris temperature
~2100°K adiabatic flame temperature

Combustion Debris	Mole Fraction
O_2	.0401
N_2	.724
H	.00598
HO_2	$.231 \times 10^{-4}$
O	.00469
OH	.00711
H_2	.00711
H_2O	.154
CO	.0306
CO_2	.0534

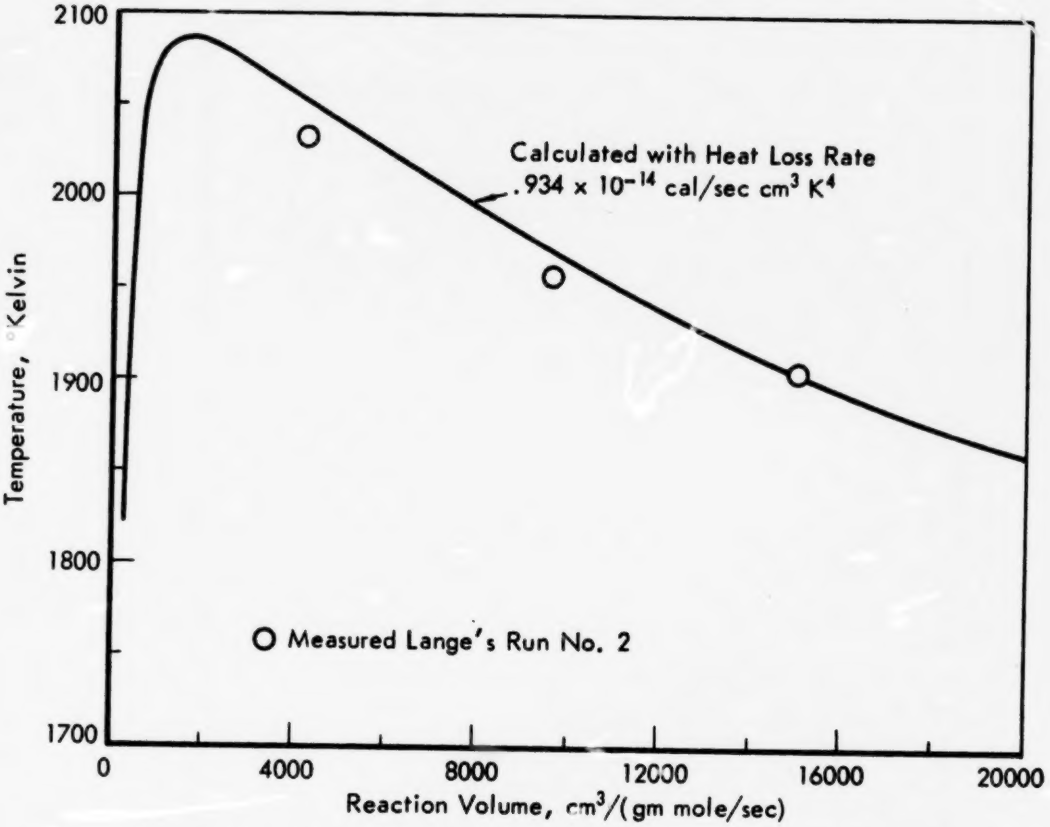


Figure 19. PREDICTED AND EXPERIMENTAL TEMPERATURES FOR COMPUTER RUN NFIX4

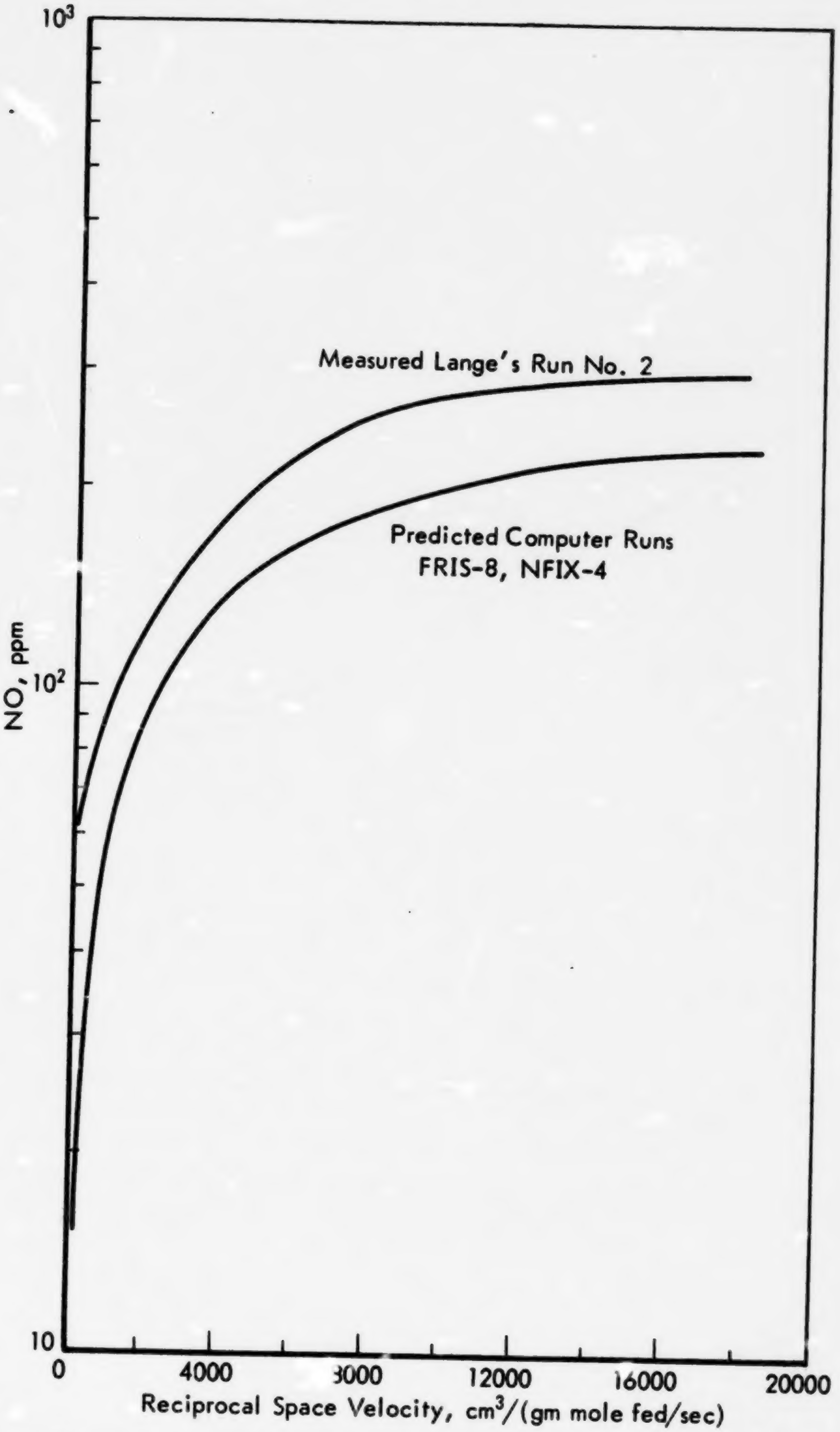


Figure 20. PREDICTED AND MEASURED NO_x PRODUCTION

form NO. Hence, one explanation of the fact that only about 40% of the chemically bound nitrogen is converted to NO may be that much of the NO formed at the char surface is reduced back, by reburning, in the CO diffusion flame surrounding the particle. An understanding of the mechanisms of reburning would help to test this conjecture. Third, the study of the mechanism of reburning should provide insight into which reactions are necessary for NO formation in diffusion flames, where the fuel-rich regime is important.

The experimental study of Wendt, Sternling, and Matovich (623) showed that reburning was effective for NO reduction and that up to 50% reduction in NO was obtained from flue gases. A recent patent of John Zink Company (641) deals with the homogeneous conversion of NO to N_2 by combustion in a fuel-rich environment.

The specific purpose of the study reported here was to answer the following critical questions:

1. Is the Zeldovich mechanism, or its reverse, adequate to explain the reduction of NO in fuel-rich combustion?
2. If not, what are the other important reactions, and what are the intermediate species?
3. What is the effect of the composition of gas mixture? Is reburning by hydrogen more or less effective than reburning by CO or hydrocarbons? What is the effect of CO_2 in the gas mixture?
4. What is the route through which the N-N bond is formed from NO?

The approach adopted was to use the kinetic mechanism shown on Table 13 as a base. This mechanism is based on the rate coefficients of Lange (544) and of Wilde (642) except for those reactions that had been investigated in the Leeds reports (786). Results shown on Table 14 indicate that according to this mechanism NO can be reduced by hydrogen. The reduction takes place in the order of 0.02 seconds.

In order to investigate which reactions and which species played a role in the NO reduction, we divided the reactions into four groups. Group 1 consisted of those reactions destroying NO, Group 2 consisted of those reactions that make N_2, Group 3 consisted of those reactions that split the NO bond (this includes the destruction of HNO), Group 4 consisted of those reactions that make N atoms. The relative importance of the reactions is shown below:

Group	Important Reactions
1	5f, 12r, 14f, 15f, 22r
2	5f, 22r
3	5f, 22r, 26r, 32r
4	5f, 6f, 7f, 26r, 29r, 30r, 31r

The reaction numbers correspond to those on Table 13, and the designation f and r denote if the reaction is going in the forward or reverse direction. This analysis led to the conclusion that the mechanism of NO reduction was as follows: Nitrogen atoms are built up by the "shuffle," or equilibrated, reactions involving HNO, NH, H, OH, H_2. These N atoms then react with NO via the reverse Zeldovich:

Table 13. REACTIONS USED IN REBURNING MODEL

1.	LDSB 1	$H_2 + O$	$= H + OH$
2.	LDSB 3	$H_2 + OH$	$= H_2O + H$
3.	LDSB 5	$H_2O + O$	$= OH + OH$
4.	LDSC 1	$O_2 + H$	$= O + OH$
5.	LDSD 1	$NO + N$	$= N_2 + O$
6.	LDSD 3	$O_2 + N$	$= NO + O$
7.	LDSD 11	$NO_2 + N$	$= NO + NO$
8.	LDSE 1	$NO_2 + O$	$= NO + O_2$
9.	LDSE 3	$NO_2 + M$	$= NO + O + M$
10.	LDSE 6	$NO + NO + O_2$	$= NO_2 + NO_2$
11.	SBOW 3	$O_2 + M$	$= O + O + M$
12.	WILD 1	$H_2 + NO$	$= HNO + H$
13.	WILD 5	$N_2O + H$	$= N_2 + OH$
14.	WILD 6	$HNO + OH$	$= NO + H_2O$
15.	WILD 7	$H + NO + M$	$= HNO + M$
16.	WILD 9	$HNO + NO$	$= N_2O + OH$
17.	WILD 10	$HNO + HNO$	$= N_2O + H_2O$
18.	WILD 11	$N_2O + M$	$= N_2 + O + M$
19.	HOMER 1	$H + OH + H_2O$	$= H_2O + H_2O$
20.	HOMER 2	$H + OH + M$	$= H_2O + M$
21.	LDSA 1	$CO + OH$	$= CO_2 + H$
22.	LANG 2	$N_2 + HO_2$	$= NO + HNO$
23.	LANG 4	$N_2 + OH$	$= N_2O + H$
24.	LANG 5	$N_2 + O_2$	$= N_2O + O$
25.	LANG 6	$N_2 + NO_2$	$= N_2O + NO$
26.	LANG 8	$N + OH$	$= NO + H$
27.	LANG 9	$N_2O + O$	$= NO + NO$
28.	LANG 10	$N_2O + O_2$	$= NO + NO_2$
29.	LANG 11	$N + OH$	$= NH + O$
30.	LANG 12	$N + H_2$	$= NH + H$
31.	LANG 13	$N + H_2O$	$= NH + OH$
32.	LANG 14	$NH + OH$	$= NO + H_2$
33.	LANG 15	$NH + O$	$= NO + H$
34.	LANG 16	$NH + OH$	$= HNO + H$
35.	LANG 17	$NH + O_2$	$= HNO + O$
36.	LANG 21	$HNO + O$	$= NO + OH$

Table 14. "NO" REDUCTION BY HYDROGEN. NO "CO_2" IN MIXTURE

Temperature 1900°K

Run	Time secs	H_2	O_2	N_2	NO	H_2O	CO	CO_2	Notes
WILD 4	0	.62	.07	.29	.02				
	.003	.473	.176(-7)	.295	.0105	.146			Complete kinetic mechanism 36 reactions $\Phi = 8.8$
	.05	.460	.761(-9)	.300	.228(-4)	.160			
	Result: NO almost completely reduced								
WILD 5	0	.62	.07	.29	.02				
	.5	.46	.80(-9)	.30	.201(-4)				Simplified kinetic mechanism; 21 reactions; $\Phi = 8.8$
	Result: same as previous run								
WILD 6	0	.38	.12	.48	.02				
	.002	.137	.102(-6)	.482	.0159				$\Phi = 1.5$ Simplified mechanism
	1.0	.12	.445(-7)	.489	.54(-4)				
	Result: NO reduced								
WILD 5A	0	.62	.07	.29	.02				
	1.6	.48	.12(-8)	.29	.1996(-1)				Zeldovich only. Conditions same as WILD 5. $\Phi = 8.8$
	Result: insignificant NO reduction								

$$N + NO = N_2 + O \qquad (66)^*$$

which is faster, under fuel-rich conditions, than

$$N + O_2 = NO + O \qquad (67)$$

because of the low O_2 concentration. It appeared, therefore, that under fuel-rich conditions there is no need for those reactions involving N_2O, NO_2, etc. A subsequent run using only 21 of the original 36 reactions confirmed this (see Table 14). The Zeldovich mechanism alone is inadequate (Table 14) because of the slow rate of formation of N atoms through

$$O + NO = N + O_2. \qquad (68)$$

Since an important application of the idea of NO reduction by reburning involves secondary fuel injection into furnace flue gases, this was simulated in the computer runs shown on Table 15. Although NO can be reduced, this appears to occur slowly and only under very fuel-rich conditions. This is in contrast to the data of Wendt et al (623) who found substantially more NO reduction with reburning in a flue gas environment. In those experiments the residence times were of the order of 0.1 seconds, indicating that the NO reduction measured was much more rapid than that predicted by this model when CO_2 is present.

According to our theoretical model of NO reduction, it appears that CO_2 acts as an inhibitor, due to the conversion of CO_2 to CO which requires consumption of H_2. Since this has not been observed in practice, it appears that our model is not complete and that possibly some reactions involving cyanides may play a role. If this is so, these cyanide reactions would essentially be the reverse of Fenimore's prompt NO reactions and might lead to substantial cyanide emissions under reburning conditions.

From this study we can reach the following conclusions:

1. The Zeldovich mechanism alone is not adequate to explain the reduction of NO under fuel-rich conditions. An expanded kinetic mechanism was found that predicted this.

2. In the absence of compounds containing carbon, the important reactions are those that build up nitrogen atoms via intermediate compounds such as HNO, NH, etc.

3. However, this model does not predict the correct rate of NO reduction in the presence of CO_2. Other reactions involving cyanides may be important.

4. The N-N bond is formed through $N + NO = N_2 + O$ (reverse Zeldovich) where the N atoms are produced through other reactions.

(*) Equation 65 intentionally omitted.

Table 15. NO REDUCTION IN PRESENCE OF CO_2

Temperature 1900°K

Run	Time secs	H_2	CO_2	H_2O	O_2	NO	N_2	CO	Notes
WILD 7	0	.123	.1	.1	.015	.022	.64	-	$\Phi = 4.1$
	.02	.038	.05	.184	.21(-6)	.0159	.643	.05	
	1.0	.029	.058	.194	.21(-6)	.0036	.651	.042	
	Result: NO reduced - but more slowly								
WILD 3	0	.026	.088	.177	.01	.01	.6890		$\Phi = 1.3$
	.03	.196(-2)	.0841	.201	.214(-4)	.0097	.689	.0039	
	.87	.126(-2)	.0854	.202	.526(-4)	.0076	.690	.00256	
	Result: NO reduced slightly								

Oxidation of Fuel Nitrogen in a Diffusion Flame

The fuels which contain large amounts of chemically bound nitrogen are coal and residual oils, both of which are usually burned in turbulent diffusion flames. An idealized mathematical model of the diffusion flame involving both the physical and chemical aspects is, therefore, expected to be a useful tool in improving our understanding of the fuel nitrogen reactions. A preliminary version of a model is described here for hydrogen fuel with bound nitrogen simulated as free nitrogen atoms. Such a model is based on the idea that reactions such as

$$CN + O = CO + N \qquad (69)$$

may be important in the flame. The model predicts the known result that the fractional conversion to NO goes up as the weight percent of N in the fuel goes down. It also predicts that conversion to NO (rather than N_2) is favored by high intensity of combustion and by high temperature.

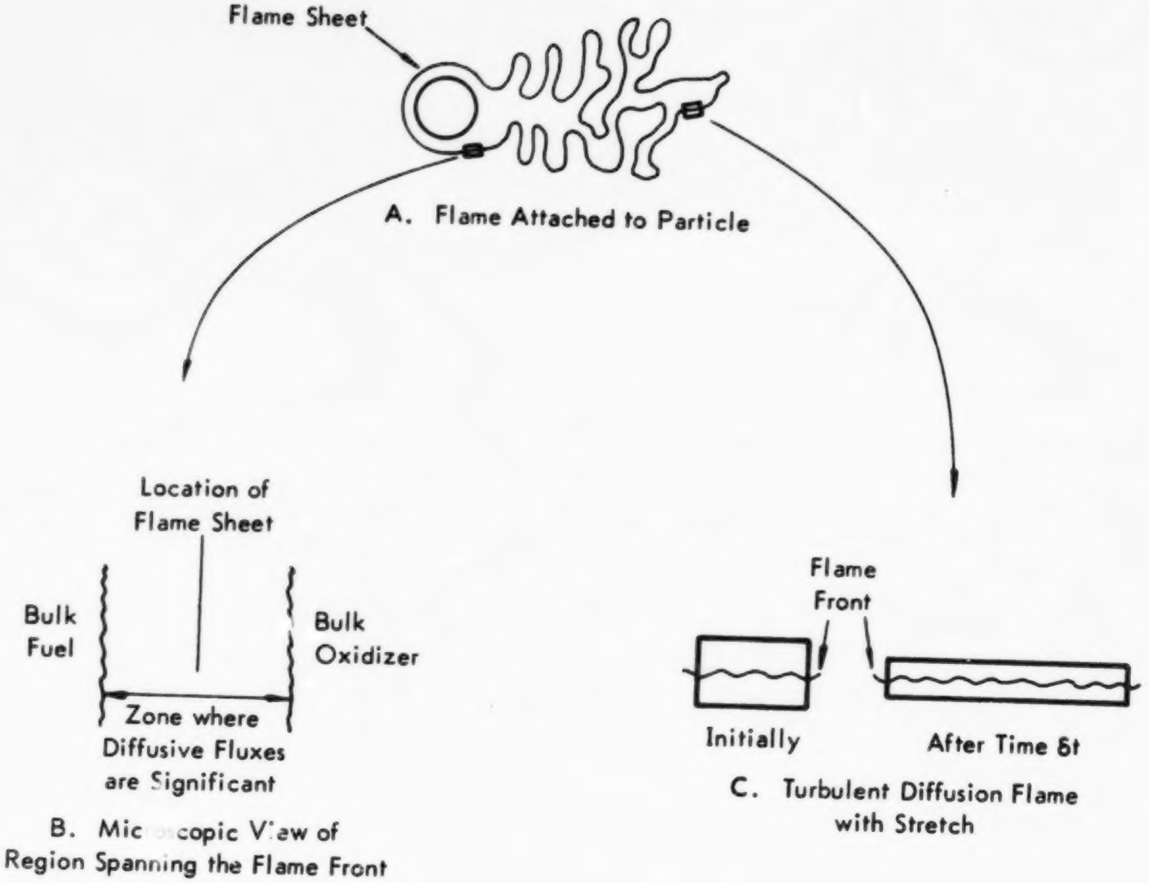
The simplest model of a diffusion flame [Burke and Schumann (789)] pictures all the combustion reactions as occurring at a flame sheet of infinitesimal thickness. The location of the flame sheet adjusts itself so that the rates of diffusion of fuel and of oxidizer up to the flame sheet are in exact stoichiometric ratio. For determining overall rates of combustion, flame lengths, flame temperatures, etc., this is a reasonably accurate picture when the combustion rates are indeed very fast compared to rates of diffusion. However, for predicting the products of combustion, the flame sheet model must be elaborated to take into account the fact that some of the combustion reactions are faster than others. For example, in burning methane, it is found that the steps leading to carbon monoxide are much faster than the combustion of CO to CO_2.

There are several ways in which the flame sheet model may be extended to permit the calculation of the products of combustion. Figure 21 shows some of the mechanistic models for representing various types of laminar and turbulent diffusion flames, both attached and separated from particles in motion. If proper ignition has occurred and if the rates of diffusion and stretching are not too great, there will be a flame sheet of small thickness somewhere between the fuel and oxidizer. Very rapid mixing can serve to "blow out" the flame so that the mixing is largely completed before combustion in which case models based on premixed flames are more appropriate than flame sheet models.

To establish approximately the conditions at a flame sheet, we will consider Model 21-b in more detail. We picture the combustion up to CO as much more rapid than the destruction of CO. Then, at the flame sheet, the rates of diffusion of fuel and of oxygen will be approximately in a ratio to satisfy the equation

$$C_nH_m + \left(\frac{n}{2} + \frac{m}{4}\right) O_2 = nCO + \frac{m}{2} H_2O \qquad (70)$$

The flame sheet will have a finite thickness such that the rate of reaction (70) is just as fast as the rate of diffusion of reactants up to the flame front and such that concentration of oxygen within the flame front is that required to make diffusion and reaction balance within the flame front. These ideas can be expressed quantitatively as follows. Referring to Figure 22, we consider five zones arranged parallel to a flame front. The bulk of the fuel and of the oxidizer gas can be considered to be uniform in composition and temperature due to the fact that the



Flame Sheet
Location of Flame Sheet
Bulk Fuel
Bulk Oxidizer
Zone where Diffusive Fluxes are Significant
Flame Front
Initially
After Time δt

A. Flame Attached to Particle

B. Microscopic View of Region Spanning the Flame Front

C. Turbulent Diffusion Flame with Stretch

Figure 21. MECHANISTIC MODELS OF FLAME SHEETS OCCURRING IN DIFFUSION FLAMES

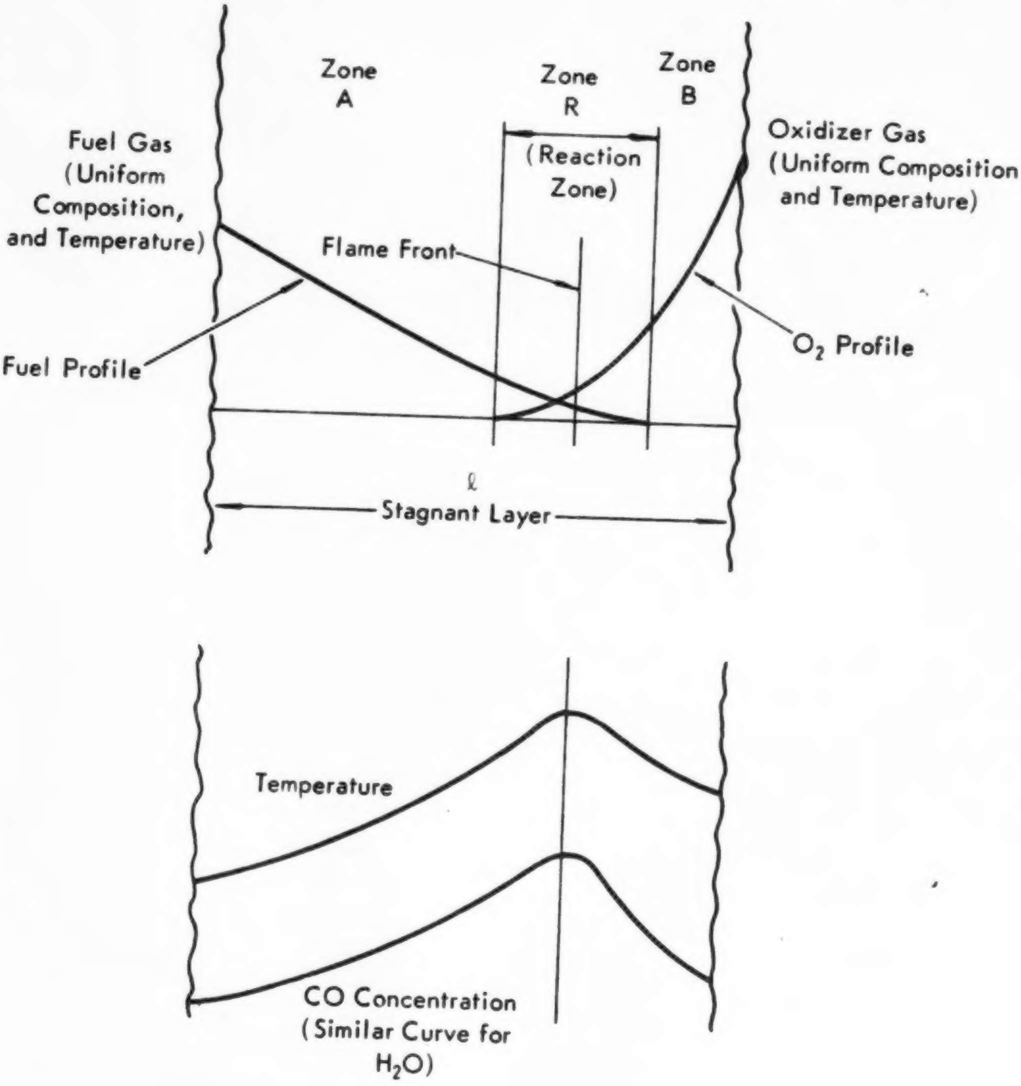

Zone
A
Zone
R
Zone
B
Fuel Gas
(Uniform
Composition,
and Temperature)
(Reaction
Zone)
Oxidizer Gas
(Uniform Composition
and Temperature)
Flame Front
Fuel Profile
O_2 Profile
ℓ
Stagnant Layer
Temperature
CO Concentration
(Similar Curve for
H_2O)

Figure 22. FLAME SHEET MODEL FOR SITUATION B

influence of the flame has not yet been felt by them. Between these two layers, the composition and temperature vary due to the diffusion and convection of heat and mass up to or away from the flame front. In Zone A, there is no oxygen and, hence, no reaction. Similarly, in Zone B there is no fuel and also no reaction. In Zone R, of small thickness relative to Zones A and B, there is reaction since both fuel and oxygen are present. The total thickness, ℓ, of Zones A, B, and R must be estimated from an appropriate model of mass transfer, such as the penetration model, the Whitman two-film model, or one of the more precise boundary layer models. For the present purposes we take ℓ to be known and assume that a steady-state calculation may be made to determine the reaction zone thickness. Under these assumptions, the following equations must be satisfied.

$$\frac{dy_i}{dx} = -N_i \sum \frac{y_j}{\rho_m D_{ij}} + y_i \sum \frac{N_j}{\rho_m D_{ij}}$$

$$\frac{dN_i}{dx} = R_i$$

$$q = \sum N_i H_i - k\frac{dT}{dx}$$

where y_i = mole fraction of species i

x = distance perpendicular to flame front, ft

N_i = molar flux of component i in the direction of increasing x, lb moles/hr ft^2

ρ_m = molar gas density, lb moles/ft^3

D_{ij} = the binary diffusion coefficient for species i in species j, ft^2/hr

R_i = the rate of formation of species i per unit volume due to chemical reactions

q = the total heat flow, in the direction of increasing x, Btu/ft^2 hr

H_i = the molar enthalpy of species i, Btu/lb mole

k = the gas thermal conductivity, Btu/hr ft °F

Neglected in this formulation is thermal diffusion.

Since we do not know the kinetic mechanisms precisely, it seems appropriate to make several approximations to make the solution to these equations more tractable and to show more clearly their physical significance. Ultimately, these approximations will be removed without, we think, altering greatly the main conclusions. We therefore take D_{ij} equal for all i and j, we take the total mass flux $N_T = \Sigma N_j$ to be zero, we take D_{ij} and k to be independent of temperature and composition, and we set $H_i = H_i^{\circ} + C_{pi}(T-T_o)$. Inside the reaction Zone R we take the profiles of mole fraction to be quadratic in x such that the value and the slope of y_i are zero at one edge of R and such that the diffusive flux at the other edge of R matches the diffusive flux in zone A or B as appropriate. We require the kinetic expressions to be satisfied in the center of the reaction zone. It can be shown with these assumptions that the thickness and O_2 concentration in the reaction zone are related to an equivalent well-stirred reactor which satisfies the following conditions

$$\frac{V\, y_{O_2}^{feed}}{F_T y_{O_2}^{prod}} = \frac{8\, t_R^2}{\rho_m D_{O_2}}$$

where t_B, the thickness of Zone B, is given by

$$t_B = \frac{\ell}{1 + \frac{\left(\frac{n}{2} + \frac{m}{4}\right) y_1 D_f}{y_2^{\ell} D_{O_2}}}$$

The other symbols are:

V/F_T = the volume per mole of feed of an equivalent well-stirred reactor representing the mid-point of the flame front, cm^3 sec/g mole
ρ_m = molar density, g mole/cm^3
D_{O_2} = diffusion coefficient of oxygen, cm^2/sec
ℓ = thickness of mass transfer boundary layer, cm
n = atoms of carbon in each fuel molecule
m = atoms of hydrogen in each fuel molecule
D_f = diffusion coefficient of fuel molecule, cm^2/sec
y_1^o = mole fraction of fuel in fuel stream
y_2^{ℓ} = mole fraction of O_2 in oxidizer stream

It can be seen from these expressions that the products initially formed at the flame front will depend on the "intensity" of combustion as defined by

$$C_I = \frac{\rho_m D(V/F_T)}{\ell}$$

High combustion intensity will lead to thick flame fronts, high O_2 concentration in the flame front, and hence will probably favor such reactions as

$$N + O_2 \longrightarrow NO + O \qquad (71)$$

over such reactions as

$$N + NO \longrightarrow N_2 + O \qquad (72)$$

Some calculations were made using this idea of the equivalent well-stirred reactor to investigate the combustion of mixtures of H_2 and HCN. The HCN, which is one of the products of pyrolysis of fuel compounds containing nitrogen, is simulated by N atoms. The kinetic scheme used is shown in Table 16. The hydrogen combustion scheme was selected to exhibit most of the known features of hydrogen flames (598). For conversion of the nitrogen atoms, only the Zeldovich reactions and the direct three-body recombination of N were used. Future studies would certainly involve more reactions.

Results are plotted in Figure 23, showing the calculated effects of combustion intensity and of temperature. Table 17 shows, in addition, the effect of fuel nitrogen level.

It is seen that the diffusion flame model predicts qualitatively the same trend of conversion with N level in the fuel as has been observed. Furthermore, it predicts an effect of combustion intensity such that more rapid combustion leads to more NO and less N_2.

This effect can be understood in terms of the competing reactions

$$N + O_2 = NO + O \qquad (73)$$

$$N + NO = N_2 + O \qquad (74)$$

Low combustion intensity leads to consumption of almost all of the O_2 in the reaction zone permitting reaction 74 to compete effectively with reaction 73.

Figure 23 also shows that low temperature favors conversion of fuel nitrogen to N_2 at least for the very simple mechanism tested. Such an effect was observed experimentally by Martin and Berkau (790). On the other hand, recirculation of flue gas, which ought to give lower combustion temperatures, was observed by Turner (791) to not change the fractional conversion of fuel nitrogen to NO.

Further work on this type of diffusion flame model should consider a more realistic set of reactions for HCN combustion and should attempt to make quantitative estimates of combustion intensity.

Table 16. REACTIONS USED IN HYDROGEN DIFFUSION FLAME

Combustion Reactions

1.	BROK 18	H_2	+ M		=	H	+ H	+ M
2.	JOHN 11	O_2	+ M		=	O	+ O	+ M
3.	HOMER 1	H	+ OH	+ H_2O	=	H_2O	+ H_2O	
4.	HOMER 2	H	+ OH	+ M	=	H_2O	+ M	
5.	BROK 4A	H	+ O_2	+ H_2O	=	HO_2	+ H_2O	
6.	BROK 4B	H	+ O_2	+ M	=	HO_2	+ M	
7.	LDSB 1	H_2	+ O		=	H	+ OH	
8.	LDSB 3	H_2	+ OH		=	H_2O	+ H	
9.	LDSB 5	H_2O	+ O		=	OH	+ OH	
10.	LDSC 1	O_2	+ H		=	O	+ OH	
11.	BROK 6	H	+ HO_2		=	OH	+ OH	
12.	THORN 1	HO_2	+ OH		=	O_2	+ H_2O	
13.	BROK 8	O	+ HO_2		=	OH	+ O_2	
14.	BROK 10	H	+ HO_2		=	H_2	+ O_2	

Reactions Involving N

15.	LDSD 1	NO	+ N		=	N_2	+ O
16.	LDSD 3	O_2	+ N		=	NO	+ O
17.		N	+ N	+ M	=	N_2	+ M

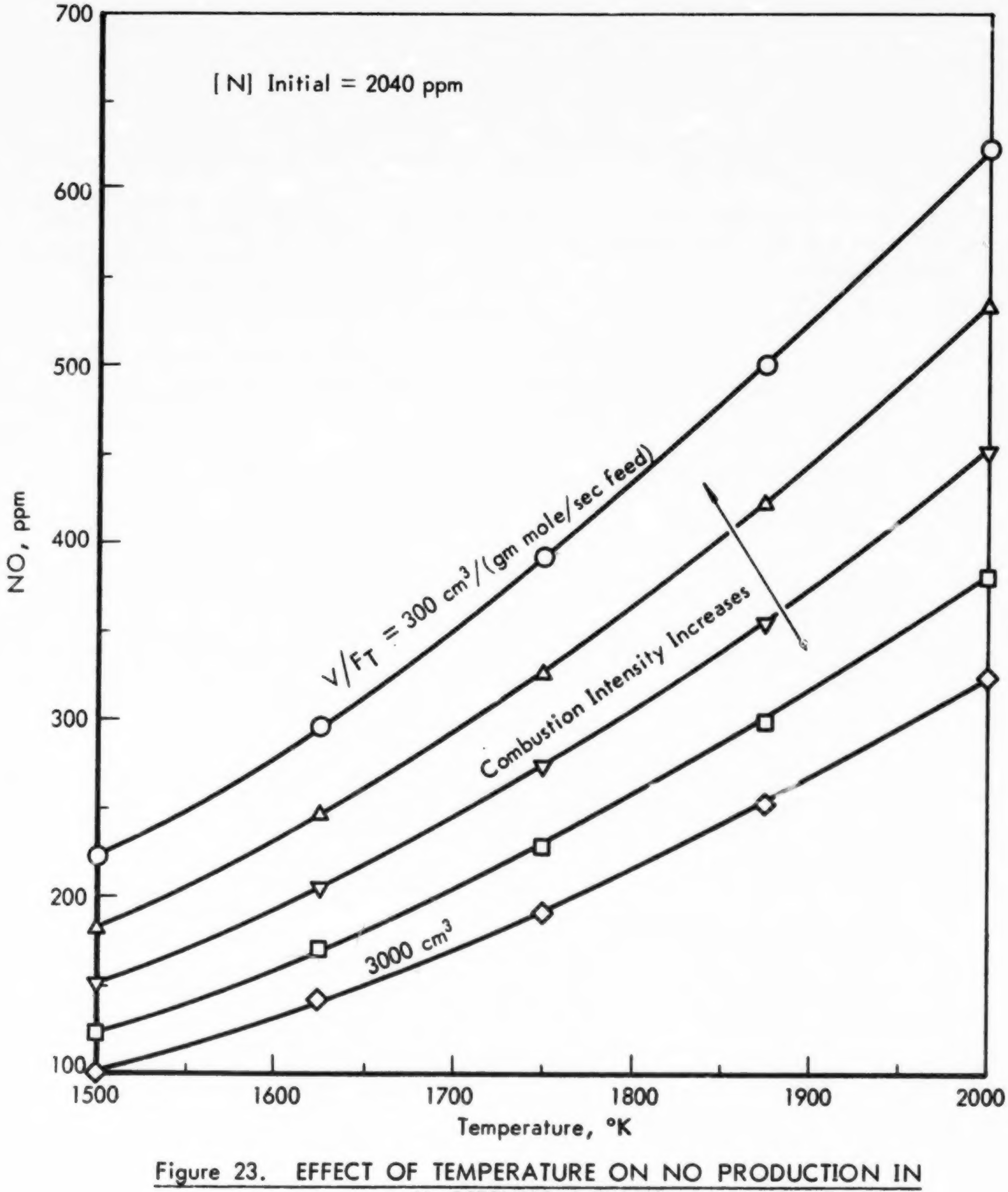


Figure 23. EFFECT OF TEMPERATURE ON NO PRODUCTION IN H_2 DIFFUSION FLAME

Table 17. CALCULATED RESULTS–HYDROGEN DIFFUSION FLAMES WITH FUEL NITROGEN SIMULATED BY N ATOMS

Atoms of Fuel N/molecule H_2		.001	.01	.03	.10
		Values of Fraction of Fuel Nitrogen Which is Converted to NO			
Temp °K	Vol cm^3/mole sec				
2000	300	73.0	21.3	9.06	3.12
	949	68.8	16.7	6.74	2.24
	3000	65.2	12.9	4.98	1.61
	9490	62.7	10.0	3.68	
	30000	61.2	7.75	2.72	
1875	300	62.7		7.38	2.49
	949	55.8		5.38	1.77
	3000	49.0		3.90	1.25
	9490	42.7		2.82	
	30000	37.3	5.74	2.03	
1750	300	57.2		5.89	1.95
	949	48.4		4.21	1.36
	3000	40.8		3.00	0.95
	9490	33.9	5.93	2.13	
	30000	27.7		1.52	

SO_2 Oxidation to SO_3 in Flames

From the literature review it was shown that a correct kinetic mechanism for the oxidation of SO_2 to SO_3 must exhibit the following features:

1. It should predict lower conversions at lower excess air;
2. It should predict superequilibrium conversions at the flame zone;
3. It should predict the proper slow decay rate;
4. It should predict negligible reaction in the absence of flames or NO;
5. It should predict the self-inhibition by SO_2 of its own oxidation;
6. It should predict the inhibition of NO on the oxidation of SO_2 in the flame zone;
7. It should predict the catalysis by NO of SO_2 oxidation in the cooler post-flame zone.
8. It should predict the effect of reburning (secondary fuel addition) which is to reduce SO_3 that has been formed.
9. It should predict typical SO_3 concentrations measured in furnace stack gases.

The approach adopted to construct such a model was to begin with the mechanism suggested by Merryman and Levy (617) as a basis and then to modify it as needed until all of the above criteria were met. For experimental data against which a model could be tested, we used the plug flow reactor data of Nettleton and Sterling (616), the flat-flame data of Wendt, Sternling, and Matovich (623), the low-temperature data of Cullis Henson and Trimm (324), the combustion data of Hedley (614), and typical data obtained from boilers and heaters.

Results Obtained From Merryman and Levy Kinetics

The basic kinetic scheme of combustion with SO_2 oxidation is shown in Table 18. Here we have taken the approach that methane fuel can be simulated by a wet CO air mixture. The rate coefficients for

$$SO_2 + O + M = SO_3 + M \qquad (75)$$

$$SO_3 + O = SO_2 + O_2 \qquad (76)$$

$$SO_3 + H = SO_2 + OH \qquad (77)$$

were those suggested by Merryman and Levy (617) in their studies of COS and H_2S flames. It can be seen that according to this mechanism SO_2 acts as a recombining catalyst for O atoms, so this route can explain why SO_2 inhibits its own oxidation, provided that the final SO_3 frozen in depends on a superequilibrium concentration of O atoms. SO_2 can also act as a recombination catalyst for H and OH through:

$$M + SO_2 + H = HSO_2 + M \qquad (78)$$

Table 18. BASIC KINETIC SCHEME FOR SO_2 OXIDATION

Reactions Used

1.	SBOW 3	$O_2 + M = O + O + M$
2.	LDSA 1	$CO + OH = CO_2 + H$
3.	LDSB 1	$H_2 + O = H + OH$
4.	LDSB 3	$H_2 + OH = H_2O + H$
5.	LDSB 5	$H_2O + O = OH + OH$
6.	LDSC 1	$O_2 + H = O + OH$
7.	MERL 1	$SO_2 + O + M = SO_3 + M$
8.	MERL 3A	$SO_3 + O = SO_2 + O_2$
9.	MERL 3B	$SO_3 + H = SO_2 + OH$
10.	HOMER 1	$H + OH + H_2O = H_2O + H_2O$
11.	HOMER 2	$H + OH + M = H_2O + M$
12.	BROK 4A	$H + O_2 + H_2O = HO_2 + H_2O$
13.	BROK 4B	$H + O_2 + M = HO_2 + M$
14.	THORN 1	$HO_2 + OH = O_2 + H_2O$
15.	JENKI 1	$H + SO_2 + M = HSO_2 + M$
16.	JENKI 2	$HSO_2 + OH = H_2O + SO_2$

followed by:

$$HSO_2 + OH = SO_2 + H_2O \qquad (79)$$

and

$$HSO_2 + H = SO_2 + H_2 \qquad (80)$$

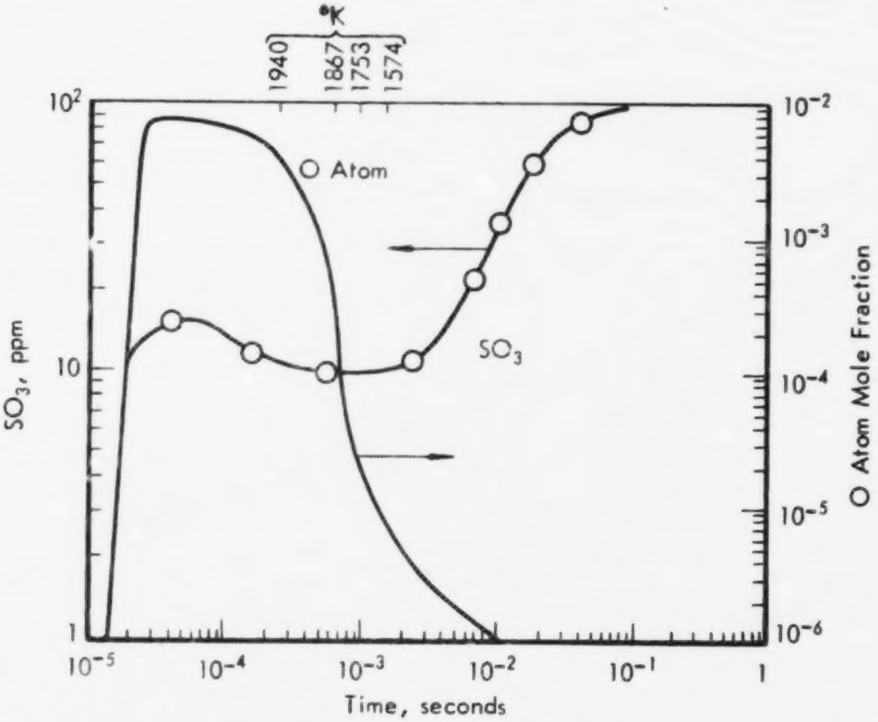
where rate coefficients for these reactions were taken from Halstead and Jenkins (639).

Preliminary computer runs were made to simulate the experiments of Nettleton and Stirling (616) in which the peak SO_3 and final SO_3 were measured in a plug flow reactor. It was shown that SO_3 does go through a maximum above its equilibrium concentration, although our calculated transient concentration was higher than that measured by a factor of three. Also, our O atom peak concentrations were suspiciously high. The final SO_3 calculated was close to that measured, although it turned out that this was also close to the equilibrium value. In Run S2 the SO_2 concentration was increased by a factor of ten, and the peak O atom concentration showed a substantial drop, indicating a substantial catalytic effect. No inhibition of SO_3 formation was observed since the final SO_3 was again at its equilibrium value. It was therefore decided to simulate the experiments of Wendt et al (623) in which this self-inhibition effect had been measured.

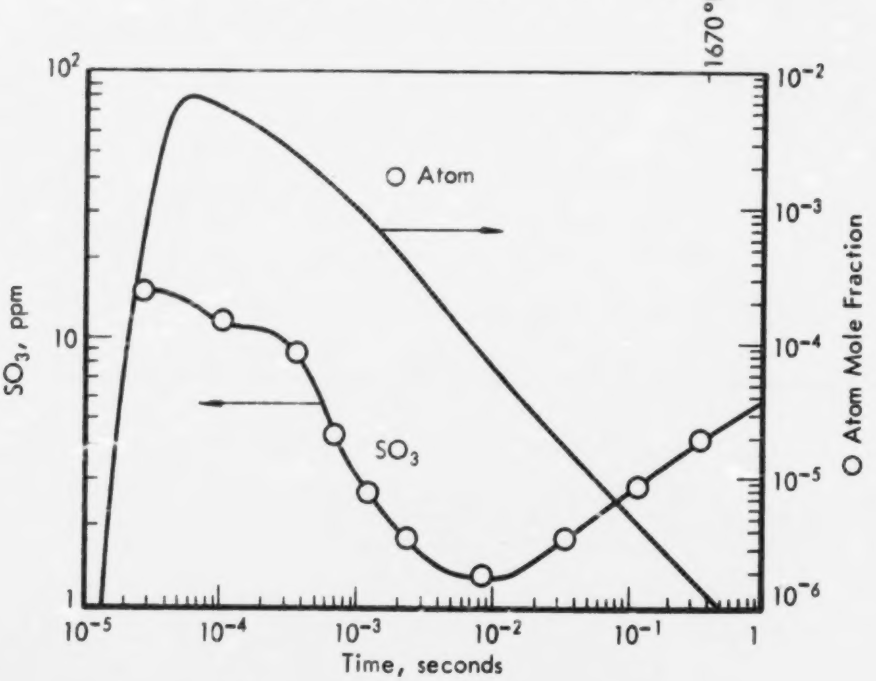
Attempts to simulate these experiments were unsuccessful, using this set of rate coefficients. In each case the SO_3 decayed back to its equilibrium value instead of being frozen in at a higher value as expected. The problem was identified as being due to the fact that reaction 75 was equilibrated at the temperatures involved, causing the SO_3 concentration to follow the O atom concentration until global equilibrium was reached. In other words, it appeared that the rate coefficients suggested by Merryman and Levy, and, incidentally, supported by the bulk of the literature, were substantially too high.

In a subsequent run, in which combustion conditions in a furnace were simulated, the SO_3 profiles obtained were unreasonable and did not fit measured plant data. Again, this was attributed to the fact that the rate coefficients used for reactions 75 through 77 were too high. Typical computed profiles for various quench rates are shown in Figure 24. These should be compared to Hedley's Figure 1. It is obvious that a substantial discrepancy exists.

Because of this discrepancy, we next compared the data of Cullis, Henson, and Trimm (342) with a simple (non-flame) homogeneous non-catalyzed SO_2 oxidation mechanism, using the same rates as used above. It was shown that rates suggested by Merryman and Levy were at least two orders of magnitude too high to agree with the data. This is demonstrated in Figure 25. Both Ladner and Pankhurst (640) and Shaw and Green (337) have published data agreeing with Cullis et al that below 1000°C the non-catalyzed SO_2 oxidation rate is extremely slow. One can only conclude that much of the data on which Merryman and Levy based their recommendation actually involved reactions of excited molecules. Such reactions can be expected to be much more rapid than straight thermal reactions; therefore, estimates for the rate of reaction 75 are much too high. It can also be argued that in order for spin conservation rules to be obeyed the forward rates of reactions 75 and 76 must have substantial activation energies.



A. T Decay 2000°K to 1000°K in 0.01 secs



B. T Decay 2000°K to 1000°K in 2 secs

Figure 24. EFFECT OF TEMPERATURE QUENCH ON SO_3 PROFILES - MERRYMAN AND LEVY KINETICS

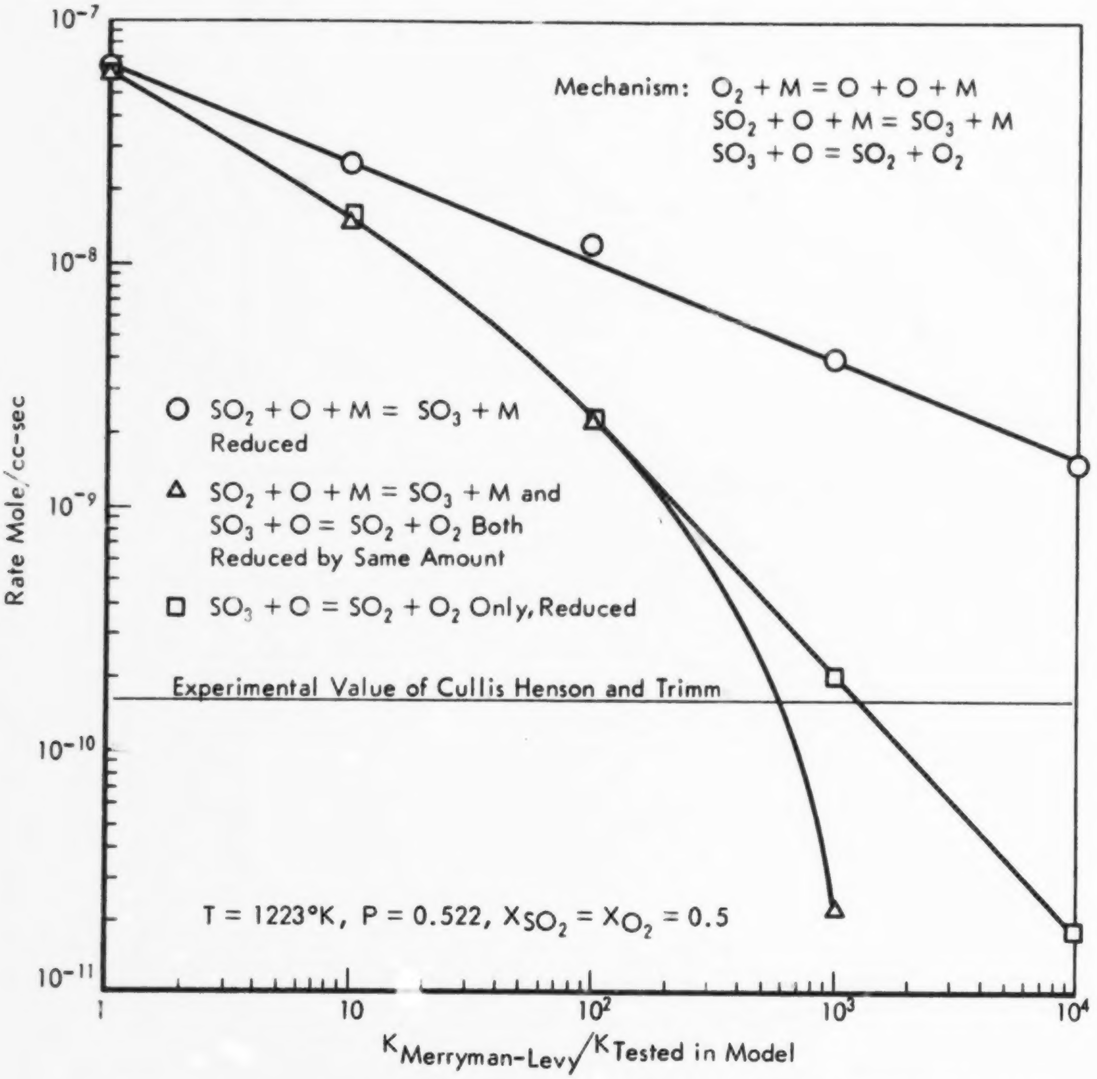


Figure 25. ATTEMPTS TO FIT MERRYMAN AND LEVY MECHANISM AND RATE COEFFICIENTS TO DATA OF CULLIS, HENSON, AND TRIMM

Results With Adjusted Rate Coefficients

Attempts were made to simulate results of Wendt et al (623), see Figure 14, in the literature review, by adjusting the activation energy and pre-exponential factor of the reaction

$$SO_2 + O + M = SO_3 + M \qquad (81)$$

It was also assumed that the rate coefficient for the reaction

$$SO_3 + O = SO_2 + O_2 \qquad (82)$$

could be given by the ratio

$$k_{81}/k_{82} = 0.857 \times 10^3 \exp(9500/RT)$$

determined by Merryman and Levy (617). The objective at this point was merely to predict the measured self-inhibition effect of SO_2 to its own oxidation. The values

$$k_{81} = 0.161 \times 10^{18} \exp(-28200/RT)$$

$$k_{82} = 0.188 \times 10^{15} \exp(-37700/RT)$$

did allow the SO_3 profile to exhibit the proper behavior, and the self-inhibition effect was observed, as shown in Table 19. The predicted conversions, however, were low by a factor of two. When the rate coefficients were raised above this value, the SO_3 decayed back to equilibrium, which was not observed experimentally. When the rate coefficients were lowered, too little SO_3 was predicted at the frozen value. These rate coefficients have unreasonably high pre-exponential factors and, as has been mentioned before, are at variance with most of the published data. Further work is necessary in order to elucidate further the mechanism of SO_2 oxidation in flames.

Conclusions

Attempts to construct a realistic model for SO_2 oxidation were unsuccessful. The rate coefficients suggested by Merryman and Levy were several orders of magnitude too high.

It was shown that SO_2 can decrease the O atom concentration by acting as a recombination catalyst.

It was shown that the self-inhibition by SO_2 on its own oxidation can be predicted by adjustment of rate coefficients. However, these adjusted rates are physically unreasonable in other respects and predict SO_3 concentrations too low by a factor of two.

More experimental and theoretical work is necessary before the effect of sulfur in flames is properly understood.

Table 19. RESULTS USING ADJUSTED RATES (SEE TEXT)

Run	Time sec	Temp °K	Mole Fractions						Notes
			CO	O_2	H_2O	O	SO_3	SO_2	
REB 1	0	1980	.082	.059	.165	0	0	.0014	Initial--low SO_2
	1.0(-4)	1979	2.9(-2)	3.4(-2)	1.4(-1)	7.9(-3)	2.2(-6)	1.39(-3)	Peak O atom
	1.3(-3)	1969	6.5(-3)	2.1(-2)	1.6(-1)	9.3(-4)	1.4(-5	1.39(-3)	Peak SO_3
	0.1	1600	1.2(-5)	1.8(-2)	1.6(-1)	2.1(-6)	7.0(-6)	1.39(-3)	Final
			Final SO_3/SO_x conversion 0.5% (Measured value = 1%)						
REB 2	0	1980	.082	.059	.165	0	0	.014	Initial--high SO_2
	8.6(-5)	1979	3.5(-2)	3.6(-2)	1.4(-1)	6.8(-3)	1.4(-5)	1.4(-2)	Peak O atom
	1.1(-3)	1970	3.96(-3)	1.97(-2)	1.6(-1)	4.77(-6)	7.97(-5)	1.39(-2)	Peak SO_3
	0.1	1600	8.5(-6)	1.8(-2)	1.648(-1)	1.4(-6)	3.6(-5)	1.396(-2)	Final
			Final SO_3/SO_x conversion 0.26%						

Synergism Between Sulfur and Nitrogen Oxides (Post-Flame Region)

The synergism between NO and SO_2 has been studied by Cullis, Henson, and Trimm (342) and by Armitage and Cullis (626). They found that at high NO concentrations (NO is the catalyst) the rate of SO_2 oxidation was second order with respect to NO and had a low activation energy. This observation is consistent with the mechanism

$$NO + NO + O_2 = NO_2 + NO_2 \qquad (83)$$

$$NO_2 + SO_2 = SO_3 + NO \qquad (84)$$

where the rates of reaction 84 have been independently measured (626), (627) and shown to be fast. At high NO concentrations (greater than 10^{-7} mole/cc) reaction 83 is controlling.

At low concentrations of NO, the SO_2 oxidation process was found to be first order in NO and to have a high activation energy. This may be explained as follows. At low NO concentrations reaction 83 is slow. Instead

$$NO + O_2 = NO_3 \qquad (85)$$

is controlling and is followed by

$$NO_3 + SO_2 = SO_3 + NO_2 \qquad (86)$$

and reaction 84 above.

It was the purpose of this study to test this mechanism against the data of Cullis et al (342) without the common steady-state assumptions. The tested model would then be used to ascertain whether the NO/SO_2 synergism plays a role in the stack gases of furnaces and sulfur plant incinerators.

One may conjecture that reaction 85 may occur without a third body, since ΔH is merely -4.58 kcal/mole, assuming NO_3 to be planar and symmetric. For NO_3 to be of this form (as compared to O-O-N-O) it is reasonable to expect the activation energy of 85 to be high, since the activated complex is three-centered and a considerable rearrangement of bonds is necessary in order for planar NO_3 to be formed. Using the data of Cullis et al, one can fit a rate coefficient for reaction 85. A value, which fits the data, is:

$$k_{85f} = 3.08 \ 10^{10} \exp(-35100/RT)$$

$$k_{85r} = 1.88 \ 10^{13} \exp(-35300/RT)$$

Comparison with the data is shown on Table 20. It should be noted that both reactions 84 and 86 are important at low NO concentrations. The difference in reaction order and temperature dependence can be attributed to the relative rates of reactions 83 and 85. This interpretation is similar to that proposed by Cullis et al with the difference that we have omitted the reaction

$$NO_3 + NO = NO_2 + NO_2 \qquad (87)$$

since it was shown by our computer runs to contribute little to the overall result. Instead, the mechanism of NO_2 formation is either by

$$NO + NO + O_2 = NO_2 + NO_2 \tag{88}$$

or

$$NO_3 + SO_2 = NO_2 + SO_3 \tag{89}$$

depending on the NO concentration and the temperature.

We have applied this synergism model to investigate whether this mechanism plays a role in the post-flame stack gases of a typical furnace and of a typical sulfur plant incinerator. For the furnace it was assumed that the flue gases were cooled from 1800°K to 600°K in two seconds. Results are shown in Table 21. Negligible SO_3 was formed, showing that this synergism is not important for this typical furnace. Two cases were considered for the sulfur plant incinerator. Case A was representative of an upset (which can let significant amounts of ammonia into the incinerator) with 3500 ppm NO in the flue gas. After two seconds, 3.4 ppm SO_3 was formed, which can be significant. At this point the formation of SO_3 was constant at 0.373 mole/cc-sec. Further details are shown in Table 21. Case B was with the sulfur plant operating normally--only 35 ppm NO in the flue gas. Then only 0.02 ppm SO_3 was formed after two seconds.

Our conclusions are that the data of Cullis, Henson, and Trimm can be modeled using a simplified mechanism and that this model indicates that the NO/SO_2 synergism is only important in combustion units when the NO concentration is in the 1000 ppm range or higher. In practice, this means that the synergism is only important in the case of upset sulfur plants.

Table 20. $NO\text{-}SO_2$ SYNERGISM

Mechanism

$$NO + NO + O_2 = NO_2 + NO_2 \tag{1}$$
$$NO_2 + SO_2 = NO + SO_3 \tag{2}$$
$$NO + O_2 = NO_3 \tag{3}$$
$$NO_3 + SO_2 = NO_2 + SO_3 \tag{4}$$

Rate Coefficients	Reference
$k_{1f} = 1.55 \times 10^{10} \exp -2200/RT$	Leeds - high temperature range
$k_{2f} = 6.31 \times 10^{12} \exp -27000/RT$	Armitage and Cullis
$k_{3f} = 3.08 \times 10^{10} \exp -35100/RT$	See text and data below
$k_{4f} = 5.32 \times 10^{12} \exp -2050/RT$	Semenov/collision rate times 0.01

Agreement with Data - Cullis, Henson, and Trimm
SO_2 conc = 3.3×10^{-6} mole/cc $O_2 = 3.3 \times 10^{-6}$ mole/cc

Initial NO conc, mol/cc	Temp °K	Time sec	SO_3, mole/cc	Rate mole/cc sec	Experimental Value of Rate, mole/cc sec
1.0×10^{-6}	1173	10.98	4.495×10^{-7}	4.1×10^{-8}	2.63×10^{-8}
1.0×10^{-6}	873	11.71	0.345×10^{-6}	2.9×10^{-8}	1.32×10^{-8}
0.025×10^{-6}	1173	22.1	19.93×10^{-9}	0.902×10^{-9}	1.05×10^{-9}
0.025×10^{-6}	873	11.58	0.325×10^{-9}	2.806×10^{-11}	2.63×10^{-11}

Table 21. APPLICATION OF MODEL FOR NO/SO_2 SYNERGISM TO FURNACE FLUE GAS AND SULFUR PLANT INCINERATOR EMISSIONS

1. Typical Furnace (Post-Flame Reactions Only)

Temperature decay: 1800°K to 600°K in two seconds
Initial Concentration (mole fractions)

SO_2	1000 ppm
NO	500 ppm
O_2	3%

Maximum SO_3 obtained	0.01 ppm
Reaction operated at	741°K
Maximum NO_2 obtained	0.05 ppm after 3.7 seconds

2. Typical Sulfur Plant Incinerator (Post-Flame Reactions Only)

A. Temperature decay: 1800°K to 922°K in 0.1 seconds
Initial Concentration

NO	3500 ppm
O_2	12%
SO_2	2%

At time 2 secs, temp 922°K

		Rate formation mole/cc-sec
SO_3	3.4 ppm	$.373 \times 10^{-10}$
SO_2	2%	
NO	3500 ppm	
NO_2	3.5 ppm	$.798 \times 10^{-11}$

B. Temperature decay: 1800°K to 922°K in 0.1 seconcs
Initial Concentrations

NO	35 ppm
O_2	12%
SO_2	2%

At time 2 secs, temp 922°K

		Rate formation mole/cc-sec
SO_3	0.02 ppm	0.15×10^{-12}
SO_2	2%	
NO	35 ppm	
NO_2	0.008 ppm	0.19×10^{-13}

Recommendations for Future Work

While many insights have been generated by the modeling studies made, much work remains to be done before a clear idea is obtained about the mechanisms governing conversion of fuel nitrogen and sulfur to pollutants. Some recommendations are given here.

1. Diffusion Flames. A mechanism should be set up for combustion of HCN and tested in the context of diffusional flame combustion to determine if combustion intensity is as important as the calculations made here indicate and to determine the roles of combustion temperature and excess air.

2. Data on the distribution of nitrogen between char and volatiles should be obtained for both coal and residual oil.

3. Model calculations should be made for combustion of nitrogenous char surrounded by a CO diffusion flame to determine how conversion of the fuel nitrogen to NO_x can be minimized. Also, experimental work is needed in this area.

4. More good data on fixation of nitrogen in premixed flames of methane, CO, and H_2 should be obtained to test the alternative explanations for the origin of prompt NO and to establish a basis for selection of a working set of rate constants for the fixation mechanism.

5. Data is required on the role of sulfur in flames and the possible inhibition of NO_x formation by SO_2. Also, more data is required to elucidate SO_2 oxidation mechanism in flames.

6. Further experimental and theoretical studies on NO reduction by H_2 and hydrocarbons and possibly ammonia are necessary to determine activation energies of the process, complete mechanism, and possible harmful emissions--such as HCN.

JOLW/CVS:vsr

NOMENCLATURE

a_i, b_i, c_i	constants in quadratic formula for mole fractions
a_f, a_r	pre-exponential factors for reaction rates
C_{pm}	molar heat capacity
C_i	concentration of species i
C_I	combustion intensity
D_{ij}	binary diffusion coefficients
D	effective diffusion coefficient
E_f, E_r	activation energy
F_T	total molar flux
h	zone thickness
H_i	enthalpy of species i
k_f, k_r	rate coefficients for reaction in forward and reverse directions
k	thermal conductivity
K_p	equilibrium constant using partial pressures in atm
ℓ	zone thickness
m	zone thickness
n_f, n_r	exponent on temperature in rate expression
N_i	molar flux per unit area of species i
N_t	total molar flux per unit area
P_i	partial pressure of species i
q	heat flux
Q_f, Q_r	steric factor in reaction rate expression
R	gas constant
R_i	rate of production of species i per unit volume due to reactions
t_B	thickness of zone
T	absolute temperature

NOMENCLATURE, contd

V	volume of reaction zone
VOL	volume of reaction zone per unit feed rate
x	distance
y_i	mole fraction of species i
z_i	molar flux fraction of species i
ΔE_f, ΔE_r	activation energy
ζ	ratio defined by equation AIII-12
ρ_m	molar density

Subscripts

i	pertaining to species i
fuel	pertaining to the species designated as "fuel"
ox	pertaining to species designated as "oxidizer"

Superscripts

in	at the reactor inlet
e	at the reactor exit
feed	in feed stream
prod	at center of diffusion flame sheet

Appendix I. Library of Reaction Rate Data

In order to facilitate the comparison of different chemical mechanisms, it is useful to put the reaction rate data into a common form. We have, therefore, punched the rate data pertinent to this study into IBM cards. Table AI-1 is a listing of all data acquired thus far. A free format system of punching is used as described in Table AI-2. References to data sources are given in Table AI-3.

Table AI-1

LISTING OF IBM CARDS FOR REACTION RATE LIBRARY

```
STOICH,   LANG1,    N2 + O= NO + N,
STOICH,   LANG2,    N2 + HO2 = NO+ HNO,
STOICH,   LANG3,    N2 + O + M = N2O + M,
STOICH,   LANG4,    N2 + OH = N2O + H,
STOICH,   LANG5,    N2 + O2 = N2O + O,
STOICH,   LANG6,    N2 + NO2 = N2O + NO,
STOICH,   LANG7,    N + O2 = NO + O,
STOICH,   LANG8,    N + OH = NO + H,
STOICH,   LANG9,    N2O + O = NO + NO,
STOICH,   LANG10,    N2O + O2 = NO + NO2,
STOICH,   LANG11,    N + OH = NH + O,
STOICH,   LANG12,    N + H2 = NH + H,
STOICH,   LANG13,    N + H2O = NH + OH,
STOICH,   LANG14,    NH + OH = NO + H2,
STOICH,   LANG15,    NH + C = NO + H,
STOICH,   LANG16,    NH + OH = HNO + H,
STOICH,   LANG17,    NH + O2 = HNO + O,
STOICH,   LANG18,    HNO + M = H + NO + M,
STOICH,   LANG19,    HNO + OH = NO + H2O,
STOICH,   LANG20,    HNO + H = NO + H2,
STOICH,   LANG21,    HNO + O = NO + OH,
FRATCO,   LANG1.    6.68E13,   1.0,   0.0,   75.230,
FRATCO,   LANG2,    7.9E10,   1.0,   0.5,   41.8,
FRATCO,   LANG3,    1.62E11,   1.0,   0.0,   3.180,
FRATCO,   LANG4,    1.18E12,   1.0,   0.0,   75.8,
FRATCO,   LANG5,    2.88E14,   1.0,   0.0,   107.8,
FRATCO,   LANG6,    4.5E14, 1.0,0.0, 84.3,
FRATCO,   LANG7,    1.41E13,   1.0,   0.0,   7.9,
FRATCO,   LANG8,    5.3E11,   1.0,   0.5,   5.62,
FRATCO,   LANG9,    6.3E14,   1.0,   0.0,   26.7,
FRATCO,   LANG10,    6.0E14,   1.0,   -1.5,   9.9,
FRATCO,   LANG11,    1.29E14,   1.0,   0.0,   18.0,
FRATCO,   LANG12,    1.32E15,   1.0,   0.0,   22.3,
FRATCO,   LANG13,    3.59E15,   1.0,   0.0,   36.6,
FRATCO,   LANG14,    1.6E12,   1.0,   0.56,   1.5,
FRATCO,   LANG15,    5.0E11,   1.0,   0.5,   5.0,
FRATCO,   LANG16,    6.44E11,   1.0,   0.0,   2.9,
FRATCO,   LANG17,    4.38E12,   1.0,   0.0,   13.0,
FRATCO,   LANG18,    1.9E16,   1.0,   0.0,   50.0,
FRATCO,   LANG19,    2.1E12,   1.0,   0.5,   0.0,
FRATCO,   LANG20,    1.4E13,   1.0,   0.0,   3.0,
FRATCO,   LANG21,    5.0E11,   1.0,   0.5,   0.0,
RRATCO,   LANG1,    1.0E13,   1.0,   0.0,   0.0,
RRATCO,   LANG2,    9.59E11,   1.0,   0.0,   2.501,
RRATCO,   LANG3,    7.25E12,   1.0,   0.0,   40.7,
RRATCO,   LANG4,    3.0E13,   1.0,   0.0,   10.77,
RRATCO,   LANG5,    5.3E14,   1.0,   0.0,   26.7,
RRATCO,   LANG6,    2.5E14,   1.0,   0.0,   50.0,
RRATCO,   LANG7,    2.95E12,   1.0,   0.0,   39.9,
RRATCO,   LANG8,    9.53E13,   1.0,   0.0,   55.0,
RRATCO,   LANG9,    1.61E13,   1.0,   0.0,   64.5,
RRATCO,   LANG10,    2.0E8,   1.0,   0.0,   3.22,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
RRATCO,   LANG11,   1.0E12,    1.0,    0.5,    0.1,
RRATCO,   LANG12,   1.0E12,    1.0,    0.68,    1.9,
RRATCO,   LANG13,   1.6E12,    1.0,    0.56,    1.5,
RRATCO,   LANG14,   2.22E15,    1.0,    0.0,    69.6,
RRATCO,   LANG15,   1.84E14,    1.0,    0.0,    71.0,
RRATCO,   LANG16,   2.0E11,    1.0,    0.5,    13.0,
RRATCO,   LANG17,   1.0E11,    1.0,    0.5,    7.0,
RRATCO,   LANG18,   3.1E15,    1.0,    0.0,    0.7,
RRATCO,   LANG19,   4.1E14,    1.0,    0.5,    71.5,
RRATCO,   LANG20,   9.5E12,    1.0,    0.0,    58.0,
RRATCO,   LANG21,   9.3E12,    1.0,    0.0,    54.5,

STOICH,SBOW 1,CH4+M=CH3+H+M ,
STOICH,SBOW 2,CH4+O2=CH3+HO2,
STOICH,SBOW 3,O2+M=O+O+M,
STOICH,SBOW 4,CH4+O=CH3+OH,
STOICH,SBOW 5,CH4+H=CH3+H2,
STOICH,SBOW 6,CH4+OH=CH3+H2O,
STOICH,SBOW 7,CH3+O=HCHO+H,
STOICH,SBOW 8,CH3+O2=HCHO+OH,
STOICH,SBOW 9,HCHO+OH=CHO+H2O,
STOICH,SBOW10,CHO+OH=CO+H2O,
STOICH,SBOW11,CO+OH=CO2+H,
STOICH,SBOW12,H+O2=O+OH,
STOICH,SBOW13,O+H2=H+OH,
STOICH,SBOW14,O+H2O=OH+OH   ,
STOICH,SBOW15,H+H2O=H2+OH,
STOICH,SBOW16,H+OH+M=H2O+M,
STOICH,SBOW18,CHO+M=H+CO+M,
FRATCO,SBOW 1,1.5E+19,1.,0.,99.594,
FRATCO,SBOW 2,1.0E+14,1.0,0.,44.946,
FRATCO,SBOW 3,3.6E+18,1.0,-1.0,117.612,
FRATCO,SBOW 4,1.7E+13,1.,0.,8.672,
FRATCO,SBOW 5,6.3E+13,1.0,0.,12.573,
FRATCO,SBOW 6,2.8E+13,1.0,0.,4.950,
FRATCO,SBOW 7,1.0E+14,1.0,0.,0.,
FRATCO,SBOW 8,1.0E+12,1.0,0.,0.,
FRATCO,SBOW 9,1.0E+14,1.0,0.,0.,
FRATCO,SBOW10,1.0E+14,1.0,0.,0.,
FRATCO,SBOW11,3.1E+11,1.0,0.,0.594,
FRATCO,SBOW12,2.2E+14,1.0,0.,16.454,
FRATCO,SBOW13,4.0E+14,1.0,0.,9.365,
FRATCO,SBOW14,8.4E+14,1.0,0.,18.058,
FRATCO,SBOW15,1.0E+14,1.0,0.,20.196,
FRATCO,SBOW16,2.00E+19,1.0,-1.0,0,
FRATCO,SBOW18,2.0E+13,1.0,0.5,28.512,
RRATCO,SBOW 1,13.34E+16,1.0,0.,-2.846,
RRATCO,SBOW 2,1.32E+12,1.0,0.,-10.724,
RRATCO,SBOW 3,14.78E+16,1.,-1.0,-0.918,
RRATCO,SBOW 4,2.8E+11,1.0,0.,8.692,
RRATCO,SBOW 5,23.56E+11,1.0,0.,14.623,
RRATCO,SBOW 6,4.72E+12,1.,0.,22.140,
RRATCO,SBOW 7,1.255E+15,1.0,0.,67.020,
RRATCO,SBOW 8,9.55E+11,1.0,0.,50.950,
RRATCO,SBOW 9,3.69E+13,1.0,0.,43.260,
RRATCO,SBOW10,2.45E+15,1.0,0.,91.590,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
RRATCO,SBOW11,4.04E+13,1.0,0.,22.924,
RRATCO,SBOW12,0.167E+14,1.0,0.,0.384,
RRATCO,SBOW13,1.762E+14,1.0,0.,7.335,
RRATCO,SBOW14,0.820E+14,1.0,0.,0.888,
RRATCO,SBOW15,0.22E+14,1.0,0.,5.056,
RRATCO,SBOW16,3.79E+20,1.0,-1.0,119.630,
RRATCO,SBOW18,2.58E+13,1.0,0.5,0.472,

STOICH,    NEWH1,    H2O+M=OH+H+M,   SYMCA-1969-12-604
FRATCO,    NEWH1,    5.4E17,1.0,0.0,123.6,
RRATCO,    NEWH1,    1.5E16,    1.0,    0.0,    0.0,
STOICH,    NEWH2,    H2+M=H+H+M,     SYMCA-1969-12-604,
FRATCO,    NEWH2,    3.1E15,    1.0,    0.0,    110.0,
RRATCO,    NEWH2,    7.0E17,    1.0,    -1.0,    0.0,
STOICH,    NEWH3,    NO+M=N+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH3,    3.989E20,    1.0,    -2.5,    150.0,
RRATCO,    NEWH3,    0.9E15,    1.0,    0.0,    0.0,
STOICH,    NEWH4,    N2+M=N+N+M,     SYMCA-1969-12-604,
FRATCO,    NEWH4,    4.754E17,    1.0,    -1.5,    224.9,
RRATCO,    NEWH4,    6.1E14,    1.0,    0.0,    0.0,
STOICH,    NEWH5,    N2O+M=N2+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH5,    1.0E15,    1.0,    0.0,    61.0,
RRATCO,    NEWH5,    1.82E13,    1.0,    0.0,    21.4,
STOICH,    NEWH6,    NO2+M=NO+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH6,    5.4E21,    1.0,    -1.0,    74.0,
RRATCO,    NEWH6,    2.0E16,    1.0,    0.0,    0.0,
STOICH,    NEWH7,    O2+M=O+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH7,    3.563E18,    1.0,    -1.0,    118.0,
RRATCO,    NEWH7,    1.0E14,    1.0,    0.0,    0.0,
STOICH,    NEWH8,    OH+H=H2+O,    SYMCA-1969-12-604,
FRATCO,    NEWH8,    1.4E12,    1.0,    0.0,    6.0,
RRATCO,    NEWH8,    3.3E12,    1.0,    0.0,    8.00,
STOICH,    NEWH9,    OH+O=O2+H,    SYMCA-1969-12-604,
FRATCO,    NEWH9,    5.5E13,    1.0,    0.0,    1.0,
RRATCO,    NEWH9,    7.2E14,    1.0,    0.0,    16.9,
STOICH,    NEWH10,    OH+H2=H2O+H,    SYMCA-1969-12-604,
FRATCO,    NEWH10,    6.2E13,    1.0,    0.0,    6.0,
RRATCO,    NEWH10,    3.2E14,    1.0,    0.0,    21.1,
STOICH,    NEWH11,    OH+OH=H2O+O,    SYMCA-1969-12-604,
FRATCO,    NEWH11,    7.7E12,    1.0,    0.0,    1.00,
RRATCO,    NEWH11,    8.3E13,    1.0,    0.0,    18.1,
STOICH,    NEWH12,    CO+OH=CO2+H,    SYMCA-1969-12-604,
FRATCO,    NEWH12,    7.1E12,    1.0,    0.0,    7.7,
RRATCO,    NEWH12,    4.7E14,    1.0,    0.0,    27.25,
STOICH,    NEWH13,    NO+O=O2+N,    SYMCA-1969-12-604,
FRATCO,    NEWH13,    3.2E9,    1.0,    1.0,    39.10,
RRATCO,    NEWH13,    13.3E9,    1.0,    1.0,    7.08,
STOICH,    NEWH14,    NO+N=N2+O,    SYMCA-1969-12-604,
FRATCO,    NEWH14,    1.55E13,    1.0,    0.0,    0.0,
RRATCO,    NEWH14,    7.0E13,    1.0,    0.0,    75.50,
STOICH,    NEWH15,    NO+O2=NO2+O,    SYMCA-1969-12-604,
FRATCO,    NEWH15,    0.18E11,    1.0,    0.5,    47.0,
RRATCO,    NEWH15,    0.58E11,    1.0,    0.5,    0.0,
STOICH,    NEWH16,    NO+NO=N2O+O,    SYMCA-1969-12-604,
FRATCO,    NEWH16,    2.6E12,    1.0,    0.0,    63.8,
RRATCO,    NEWH16,    1.42E14,    1.0,    0.0,    28.0,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
STOICH,   NEWH17,   H+O2+M=HO2+M,   SYMCA-1969-12-604,
FRATCO,   NEWH17,   1.3E15,   1.0,   0.0,   0.0,

STOICH,   CBOW1,   H2   +   O2   =   OH   +   OH,
FRATCO,   CBOW1,   2.5E12,   1.0,   0.0,   19.65,
STOICH,   CBOW2,   H   +   O2   =   OH   + O,
FRATCO,   CBOW2,   2.2E14,   1.0,   0.0,   8.45,
STOICH,   CBOW3,   O   +   H2   =   OH   +   H,
FRATCO,   CBOW3,   1.7E13,   1.0,   0.0,   4.76,
STOICH,   CBOW4,   H   +   H2O   =   H2   +   OH,
FRATCO,   CBOW4,   8.4E13,   1.0,   0.0,   10.1,
STOICH,   CBOW5,   O   +   H2O   =   OH   +   OH,
FRATCO,   CBOW5,   5.8E13,   1.0,   0.0,   9.07,
STOICH,   CBOW6,   H   +   H   +   ARGON=   H2   +   ARGON,
FRATCO,   CBOW6,   1.0E18,   1.0,   -1.0,   0.0,
STOICH,   CBOW7,   H   +   H   +   N2=   H2   +   N2,
FRATCO,   CBOW7,   1.5E18,   1.0,   -1.0,   0.0,
STOICH,   CBOW8,   O   +   O   +   ARGON=   O2   +   ARGON,
FRATCO,   CBOW8,   3.0E17,   1.0,   -1.0,   0.0,
STOICH,   CBOW9,   O   +   O   +   N2=   O2   +   N2,
FRATCO,   CBOW9,   4.0E17,   1.0,   -1.0,  0.0,
STOICH,   CBOW10,   H   +   OH   +   ARGON=   H2O   + ARGON,
FRATCO,   CBOW10,   0.20E20,   1.0,   -1.0,   0.0,
STOICH,   CBOW11,   H   +   OH   +   N2   =   H2O   +   N2,
FRATCO,   CBOW11,   0.40E20,   1.0,   -1.0,   0.0,
STOICH,   CBOW12,   H   +   OH   +   H2O   =   H2   +   H2O,
FRATCO,   CBOW12,   4.0E20,   1.0,   -1.0,   0.0,
STOICH,   CBOW13,   H   +   O2   +   ARGON   =   HO2   +   ARGON,
FRATCO,   CBOW13,   1.6E15,   1.0,   0.0,   0.504,
STOICH,   CBOW14,   H   +   O2   +   N2   =   HO2   +   N2,
FRATCO,   CBOW14,   3.0E15,   1.0,   0.0,   0.504,

STOICH,   PATT1,   CN+CN=C2+N2,     JCPSA-1962-36-1146
FRATCO,    PATT1,   1.6E15,   1.0,   0.0,   43.0

STOICH,LDSB 1,      H2       +O        =H        +OH       ,
STOICH,LDSB 3,      H2       +OH       =H2O      +H        ,
STOICH,LDSB 5,      H2O      +O        =OH       +OH       ,
STOICH,LDSB 7,      H2O      +M        =H        +OH       +M        ,
STOICH,LDSC 1,      O2       +H        =O        +OH       ,
STOICH,LDSC 3,      O2       +H        +M        =HO2      +M        ,
STOICH,LDSC 5,      H2O2     +H        =H2       +HO2      ,
STOICH,LDSC 7,      H2O2     +H        =H2O      +OH       ,
STOICH,LDSC 9,      H2O2     +OH       =H2O      +HO2      ,
STOICH,LDSC11,      H2O2     +M        =OH       +OH       +M        ,
STOICH,LDSD 1,      NO       +N        =N2       +O        ,
STOICH,LDSD 3,      O2       +N        =NO       +O        ,
STOICH,LDSD 5,      N        +O        +M        =NO       +M        ,
STOICH,LDSD 7,      N2       +O2       =NO       +NO       ,
STOICH,LDSD 9,      N2O      +O        =NO       +NO       ,
STOICH,LDSD11,      NO2      +N        =NO       +NO       ,
STOICH,LDSE 1,      NO2      +O        =NO       +O2       ,
STOICH,LDSE 3,      NO2      +M        =NO       +O        +M        ,
STOICH,LDSE 5,      NO       +O        =NO2      +HV       ,
FRATCO,LDSB 1,      1.7  E+13,1.00,0.00,9.45       ,
FRATCO,LDSB 3,      2.19 E+13,1.00,0.00,5.15       ,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
FRATCO,LDSB 5,      5.75 E+13,1.00,0.00,18.0      ,
FRATCO,LDSB 7,      3.4  E+05,1.00,0.00,0.0       ,
FRATCO,LDSC 1,      2.24 E+14,1.00,0.00,16.8      ,
FRATCO,LDSC 3,      1.59 E+15,1.00,0.00,1.0       ,
FRATCO,LDSC 5,      2.34 E+13,1.00,0.00,9.2       ,
FRATCO,LDSC 7,      3.18 E+14,1.00,0.00,9.0       ,
FRATCO,LDSC 9,      1.00 E+13,1.00,0.00,1.8       ,
FRATCO,LDSC11,      1.17 E+17,1.00,0.00,45.5      ,
FRATCO,LDSD 1,      3.10 E+13,1.00,0.00,.334      ,
FRATCO,LDSD 3,      6.43 E+09,1.00,1.00,6.25      ,
FRATCO,LDSD 5,      3.9  E+15,1.00,0.00,*********,
FRATCO,LDSD 7,      *****E+**,1.00,0.00,*********,
FRATCO,LDSD 9,      6.0  E+14,1.00,0.00,26.7      ,
FRATCO,LDSD11,      1.1  E+13,1.00,0.00,0.0       ,
FRATCO,LDSE 1,      1.0  E+13,1.00,0.00,.6        ,
FRATCO,LDSE 3,      1.1  E+16,1.00,0.00,65.0      ,
FRATCO,LDSE 5,      *****E+**,1.00,0.00,*********,
RRATCO,LDSB 1,      7.3  E+12,1.00,0.00,7.3       ,
RRATCO,LDSB 3,      5.41 E+13,1.00,0.00,20.1      ,
RRATCO,LDSB 5,      5.75 E+12,1.00,0.00,.78       ,
RRATCO,LDSB 7,      1.17 E+17,1.00,0.00,0.0       ,
RRATCO,LDSC 1,      1.3  E+13,1.00,0.00,0.00      ,
RRATCO,LDSC 3,      2.4  E+15,1.00,0.00,45.9      ,
RRATCO,LDSC 5,      9.6  E+12,1.00,0.00,24.0      ,
RRATCO,LDSC 7,      5.6  E+13,1.00,0.00,77.9      ,
RRATCO,LDSC 9,      2.8  E+13,1.00,0.00,32.7      ,
RRATCO,LDSC11,      8.4  E+14,1.00,0.00,5.3       ,
RRATCO,LDSD 1,      1.36 E+14,1.00,0.00,75.4      ,
RRATCO,LDSD 3,      1.55 E+09,1.00,1.00,38.64     ,
RRATCO,LDSD 5,      *****E+**,1.00,0.00,*********,
RRATCO,LDSD 7,      *****E+**,1.00,0.00,*********,
RRATCO,LDSD 9,      1.0  E+14,1.00,0.00,76.0      ,
RRATCO,LDSD11,      1.0  E+10,1.00,0.00,88.0      ,
RRATCO,LDSE 1,      1.0  E+12,1.00,0.00,45.5      ,
RRATCO,LDSE 3,      1.05 E+15,1.00,0.00,1.87      ,
STOICH,LDSE 6,      NO        +NO       +O2       =NO2       +NO2
FRATCO,LDSE 6,      2.4  E+09,1.00,0.00,-1.05     ,
RRATCO,LDSE 6,      4.0  E+12,1.00,0.00,26.9      ,

STOICH,WILD 1,H2+NO=HNO+H,
STOICH,WILD 3,OH+H2=H2O+H,
STOICH,WILD 5,N2O+H=N2+OH,
STOICH,WILD 6,HNO+OH=NO+H2O,
STOICH,WILD 7,H+NO+M=HNO+M,
STOICH,WILD 9,HNO+NO=N2O+OH,
STOICH,WILD10,HNO+HNO=N2O+H2O,
STOICH,WILD11,N2O+M=N2+O+M,
STOICH,WILD12,NO+NO=N2O+O,
STOICH,WILD13,O+H2=OH+H,
STOICH,WILD14,H2O+O=OH+OH,
STOICH,WILD15,H2+M=H+H+M,
STOICH,WILD17,H+OH+M=H2O+M,
STOICH,WILD20,O+NO=N+O2,
STOICH,WILD22,N+NO=N2+O,
STOICH,WILD24,H+O2=OH+O,
FRATCO,WILD 1,1.4E+13,1.0,0.0,54.9,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
FRATCO,WILD 3,3.9E+13,1.0,0.0,5.49,
FRATCO,WILD 5,3.0E+13,1.0,0.0,10.77,
FRATCO,WILD 6,2.0E+14,1.0,0.0,3.0,
FRATCO,WILD 7,3.2E+19,1.0,-1.0,00.0
FRATCO,WILD 9,2.0E+12,1.0,0.0,26.0,
FRATCO,WILD10,3.0E+11,1.0,0.0,3.5,
FRATCO,WILD11,5.0E+14,1.0,0.0,58.0,
FRATCO,WILD12,2.6E+12,1.0,0.0,63.8,
FRATCO,WILD13,1.3E+13,1.0,0.0,9.4,
FRATCO,WILD14,9.2E+13,1.0,0.0,18.0,
FRATCO,WILD15,4.2E+19,1.0,-0.84,103.2,
FRATCO,WILD17,1.8E+22,1.0,-1.5,0.0,
FRATCO,WILD20,3.2E+09,1.0,1.0,39.1,
FRATCO,WILD22,1.5E+13,1.0,0.0,0.0,
FRATCO,WILD24,9.5E+13,1.0,0.0,14.7,
RRATCO,WILD 1,7.0E+13,1.0,0.0,3.0,
RRATCO,WILD 3,1.8E+14,1.0,0.0,20.7,
RRATCO,WILD 5,1.3E+13,1.0,0.0,76.0,
RRATCO,WILD 6,6.2E+14,1.0,0.0,73.31,
RRATCO,WILD 7,1.0E+19,1.0,-1.0,46.0,
RRATCO,WILD 9,2.4E+13,1.0,0.0,41.13,
RRATCO,WILD10,1.1E+13,1.0,0.0,88.94,
RRATCO,WILD11,1.2E+13,1.0,0.0,20.77,
RRATCO,WILD12,2.0E+14,1.0,0.0,28.0,
RRATCO,WILD13,1.5E+11 ,1.0,0.0,6.95,
RRATCO,WILD14,7.6E+12,1.0,0.0,1.0,
RRATCO,WILD15,5.0E+18,1.0,-1.0,0.0,
RRATCO,WILD17,1.0E+24,1.0,-1.34,118.0,
RRATCO,WILD20,1.6E+10,1.0,1.0,7.2,
RRATCO,WILD22,6.9E+13,1.0,0.0,75.25,
RRATCO,WILD24,2.2E+12,1.0,0.0,0.0,

STOICH,   GUTM2,   N2O  ,+ O   =N2   + O2,
FRATCO,   GUTM2,   0.85E14,   1.0,   0.0,   28.0,
STOICH,   FENJ3,   N2O   + O=   NO   +   NO,
FRATCO,   FENJ3,   1.02E14,   1.0,   0.0,   28.0,
STOICH,   GUTM1,   N2O    +   ARGON=   N2   +   O   +   ARGON,
FRATCO,   GUTM1,     ,   1.0,   -4.59,   60.0,
STOICH,   MERL1,   SO2   + O   +   M   = SO3   + M,
FRATCO,   MERL1,   2.4E17,   1.0,   0.0,   2.50,
RRATCO,   MERL1 ,   11.538E+19,   1.0,   0.0,   83.090,
STOICH,   MERL3A,   SO3   +   O   = SO2   +   O2,
FRATCO,   MERL3A,   2.8E14,   1.0,   0.0,   12.0,
RRATCO,   MERL3A,   14.18E+12,   1.0,   0.0,   49.930,

STOICH,   DAVI1,  O   +   HCN   =   NCO   +   H,
FRATCO,   DAVI1,  5.2E12,   1.0,   0.0,   8.1,
STOICH,   DAVI2,   O   + CLCN   =   NCO   +   CL,
FRATCO,   DAVI2,   1.5E12,   1.0,   0.0,   6.9,
STOICH,   DAVI3,   O   +   BRCN   =   NCO   +   BR,
FRATCO,   DAVI3,   1.4E13,   1.0,   0.0,   9.7,
STOICH,   HOMER1,   H+   OH+   H2O=   H2O+   H2O
STOICH,   HOMER2,   H+   OH+   M=   H2O+   M
FRATCO,   HOMER1,   1.5E+25,   1.0,   -2.6,   0.
FRATCO,   HOMER2,   7.5E+23,   1.0,   -2.6,   0.
RRATCO,   HOMER1,   28.43E+25,   1.0,   -2.6,   119.63,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
RRATCO,   HOMER2,   1.4215E+25,   1.0,   -2.6,   119.63,
STOICH,   LDSA 1,   CO+   OH=   CO2+   H
FRATCO,   LDSA 1,   5.6E+11,   1.0,   0.0,   1.080,
RRATCO,   LDSA 1,   7.29E+13,   1.0,   0.0,   23.410,

STOICH,   BROK1,    OH+H2=H2O+H,
STOICH,   BROK2,    H+O2=OH+O,
STOICH,   BROK3,    O+H2=OH+H,
STOICH,    BROK4,    H+O2+M=HO2+M,
STOICH,   BROK5,    CO+OH=CO2+H,
STOICH,   BROK6,    H+HO2=OH+OH,
STOICH,   BROK7,    OH+HO2=H2O+O2,
STOICH,   BROK8,    O+HO2=OH+O2,
STOICH,   BROK9,    O+H2O=OH+OH,
STOICH,   BROK10,    H+HO2=H2+O2,
STOICH,   BROK11,    HO2+H2=HOOH+H,
STOICH,   BROK12,    HOOH+M=OH+OH+M,
STOICH,   BROK13,    HO2+HO2=HOOH+O2,
STOICH,   BROK14,    H+HOOH=H2O+OH,
STOICH,   BROK15,    O+HOOH=OH+HO2,
STOICH,   BROK16,    OH+HOOH=H2O+HO2,
STOICH,   BROK17,    CO+O2=CO2+O,
STOICH,   BROK18,    H2+M=H+H+M,
STOICH,   BROK19,    H+OH+M=H2O+M,
STOICH,   BROK20,    O+O+M=O2+M,
STOICH,   BROK21,    NO+HO2=NO2+OH,
STOICH,   BROK22,    NO2+H=NO+OH,
STOICH,   BROK23,    O+NO2=NO+O2,
STOICH,   BROK24,    H+NO+M=HNO+M,
STOICH,   BROK25,    H+HNO=H2+NO,
STOICH,   BROK26,    OH+HNO=H2O+NO,
STOICH,   BROK27,    O+HNO=OH+NO,
STOICH,   BROK28,    HO2+NO=HNO+O2,
STOICH,   BROK29,    O+NO+M=NO2+M,
FRATCO,   BROK1,    2.3E13,    1.0,    0.0,    5.2,
FRATCO,   BROK2,    2.04E4 ,    1.0,    0.0,    16.50,
FRATCO,   BROK3,    4.0E13,    1.0,    0.0,    10.2,
FRATCO,   BROK4,    1.0E15,    1.0,    0.0,    -1.3,
FRATCO,   BROK5,    6.6E11,    1.0,    0.0,    1.03,
FRATCO,   BROK6,    7.0E13,    1.0,    0.0,    0.0,
RRATCO,   BROK6,    0.6623E13,    1.0,    0.0,    39.62,
FRATCO,   BROK7,    6.0E12,    1.0,    0.0,    0.0,
FRATCO,   BROK8,    6.0E12,    1.0,    0.0,    0.0,
FRATCO,   BROK9,    8.4E13,    1.0,    0.0,    18.0,
FRATCO,   BROK10,    2.3E13,    1.0,    0.0,    0.0,
FRATCO,   BROK11,    1.66E13,    1.0,    0.0,    25.0,
FRATCO,   BROK12,    3.19E17,    1.0,    0.0,    47.0,
FRATCO,   BROK13,    1.8E12,    1.0,    0.0,    0.0,
FRATCO,   BROK14,    4.16E14,    1.0,    0.0,    9.00,
FRATCO,   BROK15,    8.0E13,    1.0,    0.0,    1.00,
FRATCO,   BROK16,    3.6E12,    1.0,    0.0,    0.0,
FRATCO,   BROK17,    2.5E12,    1.0,    0.0,    48.0,
FRATCO,   BROK18,    1.12E13,    1.0,    0.5,    92.6,
FRATCO,  BROK19,    1.0E19,    1.0,    -1.0,    0.0,
FRATCO,   BROK20,    8.15E18,    1.0,    -1.22,    0.0,
FRATCO,   BROK21,    1.0E13,    1.0,    0.0,    0.0,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
FRATCO,   BROK22,   7.2E14,    1.0,    0.0,    1.93,
FRATCO,   BROK23,   1.9E13,    1.0,    0.0,    1.06,
FRATCO,   BROK24,   4.0E15,    1.0,    0.0,    -0.60,
FRATCO,   BROK25,   5.0E13,    1.0,    0.0,    0.0,
FRATCO,   BROK26,   3.6E13,    1.0,    0.0,    0.0,
FRATCO,   BROK27,   3.0E13,    1.0,    0.0,    0.0,
FRATCO,   BROK28,   1.0E13,    1.0,    0.0,    0.0,
FRATCO,   BROK29,   9.4E14,    1.0,    0.0,    -1.93,

STOICH,   JOHN1,   O2+O2=O+O+O2,
FRATCO,   JOHN1,   27.52E18,    1.0,    -1.0,    118.7,
RRATCO,   JOHN1,   13.78E17,    1.0,    -1.0,    0.340,
STOICH,   JOHN2,   O2+ARGON=O+O+ARGON,
FRATCO,   JOHN2,   2.548E18,    1.0,    -1.0,    118.7,
RRATCO,   JOHN2,   1.276E17,    1.0,    -1.0,    0.340,
STOICH,   JOHN3,   O3+O3=O+O2+O3,
FRATCO,   JOHN3,   9.938E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN3,   16.79E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN4,   O+O3=O2+O2,
FRATCO,   JOHN4,   12.046E12,    1.0,    0.0,    4.79,
RRATCO,   JOHN4,   12.77E12,    1.0,    0.0,    100.6,
STOICH,   JOHN5,   O3+O2=O+O2+O2,
FRATCO,   JOHN5,   4.373E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN5,   7.388E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN6,   O3+HE=O+O2+HE,
FRATCO,   JOHN6,   3.379E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN6,   5.709E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN7,   O3+ARGON=O+O2+ARGON,
FRATCO,   JOHN7,   2.485E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN7,   4.198E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN8,   O3+N2=O+O2+N2,
FRATCO,   JOHN8,   3.876E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN8,   6.548E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN9,   O3+CO2=O+O2+CO2,
FRATCO,   JOHN9,   9.540E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN9,   16.12E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN10,   O3+H2O=O+O2+H2O,
FRATCO,   JOHN10,   38.16E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN10,   64.48E12,    1.0,    0.0,    -2.10,
STOICH,   JOHN11,   O2+M=O+O+M,
FRATCO,   JOHN11,   51.19E18,    1.0,    -1.0,    118.7,
RRATCO,   JOHN11,   25.63E17,    1.0,    -1.0,    0.340,
STOICH,   JOHN12,   O3+M=O+O2+M,
FRATCO,   JOHN12,   7.233E14,    1.0,    0.0,    22.72,
RRATCO,   JOHN12,   12.22E12,    1.0,    0.0,    -2.10,

STOICH,   PATT1,   CN+CN=C2+N2,        JCPSA-1962-36-1146
FRATCO,    PATT1,   1.6E15,    1.0,    0.0,    43.0
STOICH,   JENKI1,   H    +SO2    +M    =HSO2    +M
FRATCO,   JENKI1,   7.256E+16,    1.0,    0.0,    0.0
RRATCO,   JENKI1,   7.990E+16,    1.0,    0.0,    46.3,
STOICH,   JENKI2,   HSO2    +OH    =H2O    +SO2
FRATCO,   JENKI2,   0.6789E+14,    1.0,    0.0,    1.760
RRATCO,   JENKI2,   0.1169E+16,    1.0,    0.0,    75.09
STOICH,   ARCUL1,   NO2    +SO2    =NO    +SO3,
FRATCO,   ARCUL1,   6.31E+12,    1.0,    0.,    27.0,
```

Table AI-1 (Cont). Listing of IBM Cards for Reaction Rate Library

```
RRATCO,   ARCUL1,   38.24E+12,   1.0,   0.,   35.980,
STOICH,   PYDY16,   NO   +O2   +M   =NO3   +M,
FRATCO,   PYDY16,   3.697E+08,   1.0,   0.,   4.220,
RRATCO,   PYDY16,   2.26E+11,   1.0,   0.,   4.420,
STOICH,   PYDY29,   NO3   +NO   =NO2   +NO2 ,
FRATCO,   PYDY29,   9.216E+11,   1.0,   0.0,  -0.6,
RRATCO,   PYDY29,   3.9E+11,   1.0,   0.,   23.9,
STOICH,   SEMNO3,   NO3   +SO2   =SO3   +NO2,
FRATCO,   SEMNO3,   0.5325E+13,   1.0,   0.0,   2.050,
RRATCO,   SEMNO3,   0.1365E+14,   1.0,   0.0,   35.530,
```

Table AI-2

FORMAT FOR REACTION RATE LIBRARY

General Conventions:

1. Free format is used. That is, separate data fields on a card are enclosed within commas. A comma at the end of the card is implied.

2. Card Columns 1-6 of each card are reserved for field No. 1 which is a six-character identification word. The following three identifiers are recognized:

a. STOICH identifies the card as containing the chemical reaction written symbolically.

b. FRATCO identifies the card as containing rate data for the forward reaction.

c. pRATCO identifies the card as containing rate data for the reverse reaction.

3. Field No. 2 of each data card whether of types STOICH, FRATCO, RRATCO is used for a unique six-character name for the reaction. Blank card columns in Field No. 2 are ignored and the characters are left adjusted with blanks filling out the name on the right if fewer than six characters are used. The literature source for the rate data may be found under the reaction name in Table AI-3.

4. In punching numerical fields, the FORTRAN I, E, and F conventions are accepted but with all blank columns ignored.

Table AI-2 (Cont). Format for Reaction Rate Library

Data Card Type STOICH

Column 1-6 The characters STOICH constitute field No. 1.

Field No. 2 - the unique reaction name - up to six characters (no comma or blanks allowed).

Field No. 3 - the chemical reaction written symbolically as, for example:

$$N_2 + O = NO + N \ ,$$

Up to three reactants and up to three products can be named. Reactants and products separated by equal sign. Reactants separated from each other by + sign. Products separated from each other by + sign. Field terminated by comma. Each species name may have up to six characters (any characters allowed except + , =). When a species occurs more than once, the name must be repeated. For example, complete decomposition of ozone would be

$$O_3 = O + O + O \ ,$$

Species names are considered left adjusted with blanks ignored and with right hand side filled in with blanks. The species name M is reserved for the generalized gaseous third body.

Data Card Type FRATCO (mnemonic for Forward Rate Constants)

Field No. 1 - the six characters FRATCO

Field No. 2 - the reaction name

Fields 3, 4, 5, and 6 are used for the rate coefficients a_f, Q_f, n_f, and E_f, respectively, where

a_f = pre-exponential factor, units used are cm^3, g mole, sec, °K
Q_f = steric factor, often incorporated into a_f and hence punched as 1.0, dimensionless
n_f = an exponent on the absolute temperature, dimensionless
E_f = the activation energy, units kcal/g mole

Hence, the reaction rate for the forward reaction is calculated from

$$k_f = a_f Q_f T^{nf} \exp(-E_f/RT)$$

with T in °K and units cm^3, sec, and g moles used as appropriate.

Data Card Type RRATCO (mnemonic for Reverse Rate Constants)

Comments are the same as for FRATCO except that reference is to the reverse reaction throughout.

Table AI-3

REACTION NAMES--CONVENTIONS USED AND LITERATURE REFERENCES

General Comments

The reaction names used consist of 1 to 6 alphanumeric characters mnemonically suggestive of the authors responsible for the reaction rated followed by 1 or 2 arbitrary digits. Thus, LANG 1 is the first reaction used by Lange, H. B., Jr., preprint 28B, Sixty-Fourth Annual Meeting AIChE, San Francisco, November 28, 1971. The mnemonics and corresponding references are:

CBOW	(792)	GUTM	(403)
LANG	(544)	FENJ	(333)
LDSB	(786)	MERL	(793)
LDSC	(786)	DAVI	(385)
LDSD	(786)	HOMER	(419)
SBOW	(526)	PATT	(360)
WILD	(773)	BROK	(602
LDSE	(786)	NEWH	(720)
JOHN	(806)	ARCUL	(626)
PYDY	(729)-(747)		

The mnemonic THORN refers to unpublished Shell data while SEMN refers to estimates made using the Semenov rule and collision theory.

Appendix II. Literature References Using the CODEN System

In our literature search, a great many papers were found which are certainly relevant to a study of the fate of fuel nitrogen and sulfur but which were not used directly in the modeling studies. To facilitate reference to these papers, we have adopted the CODEN system of the ASTM (758). This system was used by Hochstim (759) in preparing his extensive compilation of reaction rate data. Given below are listings of IBM cards containing (1) an arbitrary acquisition number, (2) the periodical reference in CODEN, (3) the first author, and (4) an abbreviated title. Also given are translations of the CODEN names.

Table II-1 gives references by acquisition number
Table II-2 gives references alphabetized by author
Table II-3 gives references alphabetized by CODEN
Table II-4 gives CODEN names alphabetized by periodical name
Table II-5 gives CODEN names alphabetized by CODEN

In the case of books, preprints, etc., there is insufficient space for the full reference. Table II-6 gives these references in full; the CODEN is given simply as BOOK, PREPRINT, REPORT, etc.

In Tables II-4 and II-5 a few periodical CODEN names are assigned arbitrarily pending formal assignments by ASTM. These have * after the fifth character.

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Table AII-1

LIST OF REFERENCES IN ORDER OF ACQUISITION NUMBER

ACQ NO	CODEN REF	AUTHOR TITLE(ABBREVIATED)
00312	CBFMA-1965- -335	ANON, PARAGRAPH QUATATION FROM CONF NEWS
00313	JIFUA-1967-40-142	HEDLEY, FORMATION OF SO3 IN FLAME GASES
00314	AICPA-1968-6A	COLLINS, REVIEW OF SULFUR FLAME TECHNOLOGY
00315	IJCEA-1969-9-396	WEYCHERT ET, KINTEICS OF CAT CONVERSION OF SO2
00316	JCPSA-1963-39-275	BERKOWITZ ET, EQUIL COMPOSITION OF SULFUR VAPOR
00317	DKPCA-1967-175-647	SACHYAN ET, COMB OF DILUTE H2S FLAMES
00318	CBFMA-1967-11-150	CULLIS ET, REACTION OF SO2 AND OXGENATED RADICALS
00319	ESTHA-1969-3-63	LEVY ET, SOX FORMATION IN COS FLAMES
00320	JIFUA-1969- -188	SNOWDON ET, H2SO4 CONDENSATION FROM FLUE GASES
00321	KINFA-1969	ANON, REACTIONS OF SO,SO2, SO3 WITH H,O,OH,NO,NO2
00322	JCPAA-1967-17-800	LEVY ET, SOX FORM IN LOW P H2S FLAMES
00323	JPCHA-1968-72	WHEELER, RADICAL RECOMBINATION IN SO2 DOPED FLAMES
00324	CBFMA-1965-9-229	LEVY ET, MICROSTRUCTURE OF H2S FLAMES
00325	BUPAA-237	WEINER ET, AIR POLLUTION IN THE PULP AND PAPER IND
00326	JIFUA-1970-43-187	GUNTHER, MEAUSERMENTS OF FLAME TURBULENCE
00327	PAPWA-1968-30-786	TERRY ET, OD2 BOILER AT SCUYLKULL STATION
00328	CBFMA-1970-15-157	DURIE ET, CATALYTIC FORM OF SO3 IN FUEL RICH PROPA
00329	CBFMA-1970-15-211	ANON, S SPECIES IN BURNT GAS OF PROPANE AIR FLAMES
00330	PRLAA-1968- -380	HALSTEAD ET, CHEMILUMINESCENT REACTION OF SO
00331	CBFMA-1971-16-125	CULLIS, REACTIONS BETWEEN SO2 AND NO2
00332	PPTIA-1969-49-615	TUCKER, SOX STACK EMISSIONS-REACTIONS AND CONTROL
00333	JPCHA-1965-10-	FENIMORE ET, S IN THE BURNT GAS OF H2-O2 FLAMES
00334	TFSOA-1967-63-2442	KALLEND SO2 ON CHEMILUM AND ATOM RECOMBINATION
00335	PSRIA-1961	SUGDEN ET, OXIDES AND HYDRIDES OF N AND S IN FLAME
00336	PICMA-1963- 216	DEMARDAUCHE ET, REACTION OF S CMPDS IN FLAMES
00337	NATUA-1966- -1171	SHAW ET, OXID OF SO2 IN AIR EFFECT OF CO AND NO
00338	BBCUA-1963-27-	PANKHURST ET, FORMATION OF SO3 IN COMBUSTION
00339	JIFUA-1962-35-502	MACFARLANE, FORMATION OF SO3 IN COMBUSTION PRODUCT
00340	PRLAA- -276-461	GAYDON ET, SHOCK TUBE DECOMPOSITION OF SO2
00341	PRLAA-1958-247-123	KAUFMAN, USE OF AIR AFTERGLOW IN REACTIONS OF O
00342	PRLAA-1966-295-72	CULLIS ET, HOMOGENEOUS GAS OXIDATION OF SO2
00343	SYMCA- -12-323	MULCAHY ET, KINETICS OF O WITH SOX
00344	ZFKHA-1940-14-1428	ANON, GENERAL PHYSICAL CHEM
00345	TFSOA-1946-42-354	DOOLEY ET, OXIDATION OF SO2 IN GAS FLAMES
00346	CBFMA-1969-13-324	KALLEND, EFFECT OF SO2 ON EQUIL IN H2 FLAMES
00347	JIFUA-1970- -234	ANON, REVIEW CHEM ASPECTS OF FIRESIDE CORROSION
00348	ESTHA-1970-4-653	LEVY ET, FORMATION OF SOX IN COMBUSTION
00349	IJCEA-1969-9-317	AVERBUCH ET, ELEMENTAL S BY REDUCTION WITH NAT GAS
00350	JACSA-1947-69-3143	FENIMORE, HOMOGENEOUS REACTION OF NO AND CO
00351	PCSLA-1964- 410	CAMPBELL ET, BEHAVIOR OF CN IN ACTIVE N
00352	TFSOA-1953-49-1312	MADLEY ET, KINETICS OF OXID OF CHARCOAL WITH N2O
00353	HCACA-1930-13-629	BRINER ET, L'ACTION DES DISCH. ELECT-C2N2
00354	JACSA-1959-81-6190	GRAVEN, KINETICS OF DECOMP OF N2O AT HIGH T
00355	PRLAA-1963-272-147,	BASCO ET, CYANOGEN RADICALS BY FLASH PHOTOL
00356	JACSA-1942-64-1880	ROBERTSON ET, THERM REACTION OF H2 AND C2N2
00357	PRLAA-1965-283-302	BASCO, REACTION OF C2N2 WITH O2
00358	PRLAA-1965-283-291	BASCO ET, REACTION OF C2N2 WITH NO
00359	CBFMA-1957-1-60	COHEN ET, BURNING VELOC OF HCN IN AIR AND O2
00360	JCPSA-1962-36-1146	PATTERSON ET, KINETICS OF CN IN SHOCK WAVES
00361	IEPDA-1969-8-206	BLAKEMORE ET, PYROLYSIS OF N-BUTANE
00362	IECFA-1969-8-374	KUNUGI ET, KINETICS OF THERMAL REACTIONOF C2H4

Table AII-1 (Cont). List of References in Order of Acquisition Number

00363	JACSA-1962-84-4519	HURD ET, PYROLYSIS OF PYRIDINE, PICOLINES AND
00365	AICEA-1972-18-84	HERRIOTT ET, KINETICS OF PROPANE PYROLYSIS
00366	CJCHA-1953-31-30	INGOLD ET, THERMAL DECOMPOSITION OF BENZENE DERIVA
00367	OIGJA-1971-1-74	ANON, PROFITABILITY FACTORS IN GAS OIL CRACKING
00368	CEPRA-1969-7-71	KITZEN ET, GAS OIL PYROLYSIS IN TUBULAR REACTORS
00369	IECHA-1942-34-567	FUCHS ET, THEORY OF COAL PYROLYSIS
00370	CEPRA-1969-65-UU.65	MARSHALL ET, GAS OIL FEEDSTOCKS FO C2H4 PRODUCTI
00371	OIGJA-1971-9-94	BROOKS ET, CRACKING GAS OILS
00372	TOSCA- [illegible] -6-106	LINNELL, THERMAL DECOMPOSITION OF PYRIDINE
00373	IECHA-1942-34-567	FUCHS ET, THEORY OF COAL PYROLYSIS
00374	JAHSA-1971-28-1095	MCELROY ET, N2O, A NATURAL SOURCE OF STRAT NO
00375	JAHSA-1971-28-847	CLARK, CHEMICAL KINETICS OF CO2 ATMOSPHERES
00376	JAHSA-1971-28-833	JULIENNE ET, TEMP DEP OF CO2 ABSORPTION
00377	JAHSA-1971-28-1058	PRINN, PHOTOCHEMISTRY OF HCL IN ATM OF VENUS
00378	INCEA-1971-11-739	AKITA, FLAME PROPAGATION BASIC THEORY
00379	PRLAA-1965-288-275	SETSER ET, REACTION OF O WITH C2N2
00380	JPCAA-1971-21-713	STOCKHAM, COMPOSITION OF GLASS FURNACE EMISSSIONS
00381	JPCAA-1971-21-702	BAGWELL ET, BOILER OPERATING MODE FOR RED NOX
00382	SYMCA-1960-8-127	FENIMORE ET, RATE OF REACTION O+N2O=NO+NO
00383	SYMCA-1965-10-435	GRAY ET, H-ATOM ABSTRATION FROM N-H BONDS
00384	SYMCA-1965-10-377	ASHMORE, REVIEW ELEMENTARY COMB REACTIONS
00385	TFSOA-1968-64-1836	DAVIES ET, REACTION OF O WITH HCN, CNCL AND CNBR
00386	BSCBA-1968-77-433	AILLIET ET, BURN VEL OF C2N2 OR HCN WITH O2
00387	PRLAA-1963-273-145	HUSAIN ET, OXIDATION OF NH3 AND N2H4
00388	CBFMA-1971-17-55	SPALDING ET, CALC PROCEDURE FOR LAMINAR FLAME SPEE
00389	CBFMA-1971-16-243	CRAMAROSSA ET, OZONE DECOMP IN STEADY FLAMES
00390	ESTHA-1971-5-333	BUFALINI ET, OXID OF N-BUTANE BY PHOT OF NO2
00391	CBSTA-1971-4-17	MELVIN ET, REACTION BROADENED DIFFUSION FLAME
00392	CBSTA-1971-4-59	WESTENBERG, KINETICS OF NO AND CO IN HC FLAMES
00393	CBSTA-1971-4-73	BLUMBERG ET, NO FORMATION IN SPARK IGNITED ENGINES
00394	CBFMA-1971-17-31	HOLLAND ET, FLAME SPEED IN H2-ETHANE-N2O SYSTEM
00395	CBFMA-1971-16-237	HAY ET, OXIDATION OF GASEOUS FORMALDEHYDE
00396	CBSTA-1971-4-9	LIVESEY ET, FORMATION OF NOX IN OXY/PROPANE FLAMES
00397	JPCHA-1962-66-366	MOBERLY, SHOCK TUBE FOR HYDRAZINE DECOMPOSITION
00398	ESTHA-1971-5-39	ALTSHULLER ET, PHOTO CHEM ASPECT OF AIR POLLUTION
00399	JCPSA-1970-52-5718	GELBART ET, VIBRATIONAL RELAXATION AND DISSOSIATI
00400	CHREA-1958-58-173	CAMPBELL ET, THE HYDROGEN BROMINE SYSTEM
00401	CBFMA-1966-10-287	ROSSER ET, QUENCHING OF FLAMES BY INHIBITORS
00402	SCIEA-1971-171-1013	WESTBERG ET, CO ROLE IN PHOTCHEMICAL SMOG
00403	JPCHA-1966-70-1793	GUTMAN ET, THERMAL DECOMP OF N2O
00404	MOPHA-1966-11-403	GOGGENHEIM, DIMERIZATION OF NO, CORRECTION
00405	RIFPA-1964-19-523	JANIN ET, LA FLAMME CH4-NH3-O2
00406	JACSA-1963-85-539	STREITWIESER ET, TOLUENE IN MICROWAVE DISCHARGES
00407	PRLAA-1968-305-93	BODEN ET, EXCITATION OF CN IN ACTIVE NITROGEN
00408	MOPHA-1965-10-401	GUGGENHEIM, DIMERIZATION OF GASEOUS NO
00409	TFSOA-1967-63-1687	CERCEK ET, REACTION OF H AND OH WITH PYRIDINE
00410	BCHEA-1967-12-388	METCALFE, KINETICS OF COKE COMB IN REGENERATION
00411	JCPSA-1967-47-228	SNELLING ET, DECOMPOSITION OF N2O BY O(1D) N2
00412	CJCEA-1967-45-61	RAO ET, SHOCK TUBE STUDY OF REACT OF N2 WITH HCA
00413	CBSTA-1971-3-37	BOWMAN, NO FORMATION KINETICS, THE H2-N2-O2 REACTI
00414	JACSA-1962-84-4509	HURD ET, PYROLYTIC FORM OF ARENES, I SURVEY
00415	JOCRA-1969-45-256	BARTLE ET, TOBACCO SMOKE BY GAS CHROMATOGRAPHY
00416	CPENA-1971-79	WARD ET, OPEN FLAME FURNACE DESIGN
00417	JCPSA-1966-45-338	WESTENBERG ET, ESR AND KINETICS OF THE OD RADICAL
00418	SYMCA-1965-10-473	WESTENBERG ET, H AND O ATOM PROFILES BY ESR
00419	PRLAA-1970-314-585	HOMER ET, DISSOCIATION OF H2O IN SHOCK WAVES

Table AII-1 (Cont). List of References in Order of Acquisition Number

00420	CBSTA-1971-3-83	D'SOUZA ET, METHANE OXID IN A STEADY FLOW REACTOR
00421	SYMCA-1965-10-311	CLYNE, REACTIONS OF THE HNO MOLECULE
00422	SCIEA-1971-171-1013	WESTBERG ET, CO, ROLE IN PHOTOCHEMICAL SMOG
00423	SYMCA-1960-8-487	HICKS, DECOMP FLAME OF ETHYL NITRATE
00424	JPCHA-1968-72-3305	SAFRANY ET, REACTION OF H AND N WITH C2N2 HCN AND
00425	SYMCA-1960-8-496	GRAY ET, FLAME OF METHYL NITRITE
00426	NATUA-1964-204-988	HERZBERG ET, IDENT OF FREE RAD IN FLASH PHOTOL
00427	NATUA-1964-203-619	MCGRATH ET, UV ABS SPECTRUM OF FREE FULMINATE
00428	JPCHA-1969-73-2555	ASMUS ET, PYROLYSIS KINETICS OF ACETONITRILE
00429	CENEA-1971-6-15	ANON, DMN IN CIGARETTE SMOKE
00430	FUELS-1969-48-297	KARN ET, COAL PYROLYSIS USING LASER IRRADIATION
00431	ACIEA-1970-9-181	BROWN ET, CHEM BEHAVIOR OF ACTIVE NTTROGEN
00432	SCIEA-1971-174-1341	ARCHER ET, ENVIRONMENTAL NITROSO CMPDS
00433	RADCA- -2-142	MANI ET, REACTION OF O WITH BENZENE AND OTHER CMPD
00501	TFSOA-1956-52-1475	BULEWICZ ET, DISSOCIATION CONSTS BY FLAME PHOTOMET
00502	TFSOA-1956-52-1465	SUGDEN, DISSOCIATION CONSTS BY FLAME PHOTOMETRY I
00503	PRLAA-1956-235-89	BULEWICZ ET, HYDROGEN ATOMS IN BURNT GAS MIXTURES
00504	IJCKA-1969-1-105	KONDRATIEV ET, INTERACTION OF CO AND O
00505	JCPSA-1962-36-2582	WRAY ET, KINETICS OF NO AT HIGH TEMPERATURE
00506	JCPSA-1955-23-2399	BROMBERG ET, OXIDATION OF CH4 WITH NO2
00507	PYDYA-1965-3-197	CHINITZ, ANALYSIS OF CH4 AIR COMBUSTION
00508	ARPLA-1967-18-261	FRANKLIN, KINETICS OF HYDROCARBON COMBUSTION
00509	PYDYA-1966-4-119	CHINITZ ET, NON EQUIL HYDROCARBON AIR COMBUSTION
00510	CESCA-1963-18-177	BOWEN ET, QSS APPROXIMATION IN CHEMICAL KINETICS
00511	IECHA-1955-47-972	GERHARD ET, PHOTOCHEMICAL OXIDATION OF SO2
00512	JCPSA-1958-29-456	ANON,
00513	TFSOA-1967-63-662	GILES ET, REACTIONS OF RF3 RADICALS WITH ORGANIC H
00514	CHREA-1960-93-3014	ECKLING ET, KIN STUD. PHOTOCHLORINATION
00515	JCPSA-1965-43-3237	GETZINGER ET, RECOMBINATION H+O2+M=HO2+M
00516	JCPSA-1965-43-3371	WONG ET, REACTIONS OF O ATOMS WITH H2 AND NH3
00517	JCPSA-1967-46-4843	STUCKEY ET, REACTIONS OF O ATOMS WITH CYCLO PARAFF
00519	SYMCA-1965-10-43	WESTENBERG ET, H AND O ATOM PROFILES BY ESR IN C2
00520	JPCHA-1959-63-1834	FENIMORE ET, CONSUMPTION OF O2 IN HC FLAMES
00521	JCPSA-1969-50-2512	WESTENBERG ET, RATE COEFFICIENTS OF O + H2 AND
00522	JACSA-1951-73-15	RALEY ET, OXIDATION OF FREE CH3
00523	TFSOA-1957-53-1102	HOARE ET, REACTION OF CH3 WITH O2 AND COMPARISON
00524	JACSA-1959-81-769	SLEPPY ET, METHYL O2 AND METHYL NO REACTIONS
00525	CBFMA-1971-16-311	LIFSHITZ ET, SHOCK TUBE FOR IGN OF CH4-O2-ARGON MI
00526	CBFMA-1970-14-37	SEERY ET, METHANE OXIDATION BEHIND SHOCK WAVES
00527	ZFKHA-1959-33-572	NIKITIN, THERMAL DISSOCIATION OF DIATOMIC MOLECULE
00528	PRLAA-1970-316-539	CLARK ET, KINETICS OF N WITH O2(3SG-) AND (1DG)
00529	PRLAA-1970-316-575	HALSTEAD ET, REACTION OF H WITH C2H4
00530	CBSTA-1970-1-461	MARTENEY, KINETICS OF FORM OF NO IN HC AIR COMBUST
00533	PRLAA- -276-324	SEAKINS ET, KINETICS OF GAS PHASE HC OXIDATIONS
00534	CBSTA-1970-1-313	LAVOIE ET, NO FORMATION IN IC ENGINES
00535	SYMCA-1969-12-603	NEWHALL, ENGINE GENERATED NOX AND CO
00536	NATUA-1960-186-551	SIMONS, VIBRATIONALLY HOT MOLECULES IN RADICAL REA
00537	APMPA-1968-20	BERGER ET, REACTIONS OF SOX IN STACK PLUMES
00538	PLSSA-1967-15-643	SCHOFIELD, KINETIC RATE DATA OF ATM INTEREST
00539	SAUPA-1969-690518	TRUMPY ET, PREKNOCK KINETICS IN AN SI ENGINE
00540	PYDYA-1967-5-74	BAHN ET, REACTIONS INVOLVING N AND O
00541	JPCAA-1971-21-702	BAGWELL ET, BOILER OPERATING MODES FOR REDUCED NOX
00542	ACPYA-1946-21-576	ZELDOVICH, OXIDATION OF N2 IN COMB AND EXPLOSIONS
00544	AICPA-1971-SF-28B	LANGE NOX FORMATION IN PREMIXED COMBUSTION
00545	CBSTA-1971-4-59	WESTENBERG, KINETICS OF NO AND CO IN LEAN FLAMES
00546	JPCAA-1970-20-377	HARDISON, CONTROLLING OXIDES OF NITROGEN

Table AII-1 (Cont). List of References in Order of Acquisition Number

00547	ASMSA-1959-A-308	JEFFERIS,ET, EFFECT OF OPERATING VARB ON EMISSION
00550	SAUPA-1970-700470	CARR ET, INFLUENCE OF FUEL COMPOSITION ON CO AND
00551	CBSTA-1971-3-53	CARETTO ET, ROLE OF KINETICS IN EMISSION OF NO
00552	JEPOA-1971- -333	STARKMAN ET, ROLE OF CHEMISTRY IN GAS TURBINE EMIS
00554	ESTHA-1971-4-320	HALL ET, NOX CONTROLFROM STATIONARY SOURCES
00555	AGPTA-1964	WEIL, STUDY OF POROUS PLATE FLAMEHOLDERS
00556	JEPOA-1971- -293	TOMANY ET, NOX CONTROL TECHNOLOGY AND DEVELOPMENT
00557	PAPWA-1970-32-683	BAGWELL ET, NOX REDUCTION PROGRAM FOR OIL AND GAS
00558	CIEAA-1970	BOWMAN, NOX FORMATION IN COMB, THE H2-O2-N2 REACT
00559	CEPRA-1971-67-62	BARTOK ET, CONTROL OF NOX EMISSIONS FROM STATIONA
00560	SAUPA-1970-700708	CORNELIUS ET, FORMATION AND CONTROL OF NOX
00561	SAUPA-1971-710158	MUZIO ET, EFFECT OF T ON FORMATION OF NOX
00562	SAUPA-1971-710009	QUADER, INTAKE CHARGE DILUTION AND NOX EMISSION
00563	SAUPA-1969-690018	NICHOLLS ET, WATER INJECTION FOR CONTROL OF NOX
00564	SAUPA-1971-710011	HEYWOOD ET, PREDICTION OF NOX IN SI ENGINE EMISSI
00565	CBFMA-1970-15-97	LAVOIE, SPECTROSCOPIC MEAS OF NO IN SI ENGINES
00566	CBFMA-1970-14-325	OPSAHL ET, OSCILLATORY COMBUSTION AND POLLUTANTS
00567	JIFUA-1970- -295	SAKAI ET, COMB OF ATOMIZED FUEL OIL DROPS
00568	JIFUA-1970- -301	NURUZZAMAN ET, COMB OF MONOSIZED DROP STREAMS
00569	IEPDA-1971-10-297	SATCUNANATHAN, IGNITION DELAY OF DROPS
00570	IEPDA-1971-10-357	KUMAR ET, PNEUMATIC ATOMIZATION
00571	JIFUA-1970- -517	GIBSON, COMB OF SOLID PART IN STREAM WITH RECIRCU
00572	JIFUA-1970- -397	ARCHER ET, MULTISTAGE COMBUSTION PART 1
00573	JIFUA-1971- -196	SPALDING, COMBUSTION AS APPLIED TO ENGINEERING
00574	JIFUA-1971- -38	HEDLEY ET, COMBUSTION OF SINGLE DROPS ANS SPRAYS
00575	CEPRA-1971-67-57	DEMAREST, STATUS OF REACTOR FURNACES
00576	CESCA-1970-25-623	LONG ET, SELF-IGNITION OF FUEL DROPS IN HOT GASES
00577	ICONA-1970- -314	RAO ET, STIRRING BY COLD MODEL SIMULATION
00579	NAFTA-1970- -11.1	CHERADAME, THE AERODYNAMICS OF FLAMES
00580	CEPRA-1965-61-A56	KARLOVITZ, FLOW PHEN AND FLAME TECHNOLOGY
00582	JFLSA-1970-40-401	WILLIAMS, APPROACH TO FLAME TURBULENCE
00583	SCPOA-1970-58-161	COTTON, THE STRUCTURE OF FLAMES
00584	SYMCA-1953-4-267	FRISTROM ET, T PROFILES IN PROPANE-AIR FLAMES
00585	SYMCA-1971-13-997	TSUJI ET, COUNTERFLOW DIFFUSION FLAMES
00586	SYMCA-1967-11 -1057	GRAY ET, PRESENT POSITION IN EXPLOSION THEORY
00587	CBFMA-1960-4-161	WESTENBERG ET, THEORY OF LAMINAR SPHERICAL PREM
00588	SYMCA-1956-6-20	LINNETT ET, LIMITS OF INFLAMMABILITY
00589	CBFMA-1961-5-11	SPALDING ET, PROPAGATION OF STEADY LAM FLAMES
00590	CBFMA-1960-4-325	BERLAD ET, THEORY OF FLAME EXTINCTION LIMITS
00591	JASCA-1952-74-739	COOLEY ET, BURNING VELOCITY IN H2 BR2 FLAMES
00592	CBFMA-1964-8-343	VAN TIGGELEN ET, FLAMMABILITY LIMITS
00593	PRLAA-1957-240-83	SPALDING, FLAMM LIMITS AND FLAME QUENCHING
00594	SYMCA-1958-7-475	DIXON-LEWIS ET, LIMITS OF INFLAMMABILITY
00595	JCPSA-1955-23-1360	FRISTROM, ONE-DIMENSIONAL FLAME FRONT MODELS
00596	NACRA-1954-1158	DUGGER ET, PREDICTION OF FLAME VELOCITIES
00597	PRLAA-1970-317-227	DIXON-LEWIS ET, EXPT FUEL RICH H2 O2 N2 FLAME
00598	PRLAA-1970-317-235	DIXON-LEWIS, MECHANISM H2 O2 N2 FLAME
00599	PTRSA-1956-A249-1	SPALDING, THEORY OF FLAMES WITH CHAIN REACION
00600	PRLAA- -298-495	DIXON LEWIS, CONSERVATION EQUATIONS FOR FLAMES
00601	PRLAA-1968-307-111	DIXON-LEWIS, TRANSPORT PHEN IN FLAMES
00602	NASCA-1970-TND7024	BROKAW ET, CO OXIDATION IN AUTO EXHAUST
00611	TASMA-1958-80-225	MARLOW,
00612	REGTA-1965-4-1117	DE LACHAUX,
00613	TASMA-1958-80-1231	ANDERSON ET,
00614	BOOK-1963-204	JOHNSON, MECHANISM OF CORROSION BY FUEL IMPURITIES
00615	JEFPA-1966-88-165	BARRET ET,

Table AII-1 (Cont). List of References in Order of Acquisition Number

00616	SYMCA-1969-12-635	NETTLETON ET, FORMATION AND DECOMP OF SO3
00617	SYMCA-1971-13-427	MERRYMAN ET, SO3 FLAME CHEMISTRY- H2S/COS FLAMES
00618	JIFUA-1965-87-374	LEVY ET,
00619	JIFUA-1965-29-322	CRUMLEY ET,
00620	JIFUA-1956-29-372	RENDLE ET,
00621	JIFUA-1967-40-342	CROSSLEY
00622	BOOK-1963- -228	JOHNSON, MECHANISM OF CORROSION BY FUEL IMPURIITES
00623	SYMCA-1972	WENDT ET, REDUCTION OF SO3 AND NOX BY SEC FUEL
00624	JEFPA-1967-89-283	REID,
00625	BOOK-1963- -195	JOHNSON, MECHANISM OF CORROSION BY FUEL IMPURIITES
00626	CBFMA-1971-16-125	ARMITAGE ET, STUDIES OF REACTION OF NO2 AND SO2
00627	ZFKHA-1940-14-1428	BOREKOV ET, KINETICS OF REACTION OF NO2 AND SO2
00628	OIGTA-1966-NOV-66	MUNROE,
00629	COMBA-1963-JAN-MAR	GLAUBITZ,
00630	MEENA-1960-82-93	AUSTEN ET,
00631	MEENA -1960-82-92	COYKENDALL,
00633	JIFUA-1953-26-122	FLINT, METAL ADDITIVES
00634	JIFUA-1969-42-67	LEE ET,
00635	TFSOA-1966-62-2150	JOFFE ET,
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00639	TFSOA-1969-65-3013,	HALSTEAD ET,
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00702	IJCKA-1969-1-29	BENSON ET, ICL AS SOURCE OF CL, CL WITH H2
00703	IJCKA-1969-1-3	FRANKLIN ET, BOND ENERGIRES IN CHLOROETHANES
00704	IJCKA-1971-3-467	KREZENSKI ET, REACTIONS O(3P) WITH O3 AND COS
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00706	VGBGA-1969-1133	NIEPENBERG, DESIGN FEATURES OF GAS BURNERS
00707	JAMCA-1971- -756	PLATTEN ET, DEFLECTED TURBULENT JET FLOWS
00708	JHTRA-1971- -365	RAMSEY ET, HEATED JET IN DEFLECTING STREAM
00709	SYMCA-1963-9-7	BECKER ET, MIXING AND FLOW DUCTED TURBULENT JETS
00710	JIFUA-1961- -494	THRING, TURBULENT DIFFUSION COMBUSTION, SURVEY IJ
00711	JIFUA-1970- -517	GIBSON ET, MODEL OF COMBUSTION OF SOLID PARTICLES
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00721	SYMCA-1971-13-373	FENIMORE, FORMATION OF NO IN PREMIXED HC FLAMES
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00730	PYDYA-1968-6-101	BAHN, CHEMICAL KINETICS H+CO2=OH+CO AND
00731	PYDYA-1968-6-187	BAHN, CHEMICAL KINETICS CO2 CO HCO
00732	PYDYA-1968-6-355	BAHN, CHEMICAL KINETICS CO AND HCO
00733	PYDYA-1964-1-147	BAHN, CHEMICAL KINETICS N2 O2 NO N AND O
00734	PYDYA-1965-3-245	BAHN, CHEMICAL KINETICS H2O HO2 H2O2 O3

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00735	PYDYA-1965-2-315	BAHN, CHEMICAL KINETICS H20 HO2 O3 WITH
00736	PYDYA-1965-2-197	BAHN, CHEMICAL KINETICS H2 O2 OH H AND O
00737	PYDYA-1965-2-91	BAHN, CHEMICAL KINETICS NO3 N2O NO2 O3 O2 NO N
00738	PYDYA-1967-5-221	BAHN, CHEMICAL KINETICS REACTIONS OF O AND H
00739	PYDYA-1966-4-211	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
00740	PYDYA-1966-4-63	BAHN, CHEMICAL KINETICS N2 N H2 H NH NH2 NH3
00741	PYDYA-1966-4-57	WECKER ET, ON THE FOUR CENTER AIR REACTION
00743	PYDYA-1966-4-371	BAHN, CHEMICAL KINETICS F CL H O N SYSTEM
00744	PYDYA-1966-4-305	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
00746	PYDYA,1964-1-271	BAHN, CHEMICAL KINETICS N2O NO2 O3
00747	PYDYA-1964-1-335	BAHN, CHEMICAL KINETICS N2O NO2 O3
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00768	CBFMA-1967-11-109	GRAY ET, COMB OF H2 AND O2 WITH NH3 AND N2O
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00730	PYDYA-1968-6-101	BAHN, CHEMICAL KINETICS H+CO2=OH+CO AND
00731	PYDYA-1968-6-187	BAHN, CHEMICAL KINETICS CO2 CO HCO
00732	PYDYA-1968-6-355	BAHN, CHEMICAL KINETICS CO AND HCO
00733	PYDYA-1964-1-147	BAHN, CHEMICAL KINETICS N2 O2 NO N AND O
00734	PYDYA-1965-3-245	BAHN, CHEMICAL KINETICS H2O HO2 H2O2 O3
00735	PYDYA-1965-2-315	BAHN, CHEMICAL KINETICS H2O HO2 O3 WITH
00736	PYDYA-1965-2-197	BAHN, CHEMICAL KINETICS H2 O2 OH H AND O
00737	PYDYA-1965-2-91	BAHN, CHEMICAL KINETICS NO3 N2O NO2 O3 O2 NO N
00738	PYDYA-1967-5-221	BAHN, CHEMICAL KINETICS REACTIONS OF O AND H
00739	PYDYA-1966-4-211	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
00740	PYDYA-1966-4-63	BAHN, CHEMICAL KINETICS N2 N H2 H NH NH2 NH3
00743	PYDYA-1966-4-371	BAHN, CHEMICAL KINETICS F CL H O N SYSTEM
00744	PYDYA-1966-4-305	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
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Table AII-3

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00558	CIEAA-1970	BOWMAN, NOX FORMATION IN COMB, THE H2-O2-N2 REACT
00366	CJCHA-1953-31-30	INGOLD ET, THERMAL DECOMPOSITION OF BENZENE DERIVA
00412	CJCEA-1967-45-61	RAO ET, SHOCK TUBE STUDY OF REACT OF N2 WITH HCA
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00416	CPENA-1971-79	WARD ET, OPEN FLAME FURNACE DESIGN
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00319	ESTHA-1969-3-63	LEVY ET, SOX FORMATION IN COS FLAMES
00348	ESTHA-1970-4-653	LEVY ET, FORMATION OF SOX IN COMBUSTION
00390	ESTHA-1971-5-333	BUFALINI ET, OXID OF N-BUTANE BY PHOT OF NO2
00398	ESTHA-1971-5-39	ALTSHULLER ET, PHOTO CHEM ASPECT OF AIR POLLUTION
00554	ESTHA-1971-4-320	HALL ET, NOX CONTROLFROM STATIONARY SOURCES
00794	ESTHA-1969-3-63	LEVY ET, SOX FORMATION COS FLAME
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00353	HCACA-1930-13-629	BRINER ET, L'ACTION DES DISCH. ELECT-C2N2
00577	ICONA-1970- -314	RAO ET, STIRRING BY COLD MODEL SIMULATION
00362	IECFA-1969-8-374	KUNUGI ET, KINETICS OF THERMAL REACTIONOF C2H4
00369	IECHA-1942-34-567	FUCHS ET, THEORY OF COAL PYROLYSIS
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00504	IJCKA-1969-1-105	KONDRATIEV ET, INTERACTION OF CO AND O
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00702	IJCKA-1969-1-29	BENSON ET, ICL AS SOURCE OF CL, CL WITH H2
00703	IJCKA-1969-1-3	FRANKLIN ET, BOND ENERGIRES IN CHLOROETHANES
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00376	JAHSA-1971-28-833	JULIENNE ET, TEMP DEP OF CO2 ABSORPTION
00377	JAHSA-1971-28-1058	PRINN, PHOTOCHEMISTRY OF HCL IN ATM OF VENUS
00707	JAMCA-1971- -756	PLATTEN ET, DEFLECTED TURBULENT JET FLOWS
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00411	JCPSA-1967-47-228	SNELLING ET, DECOMPOSITION OF N2O BY O(1D) N2
00417	JCPSA-1966-45-338	WESTENBERG ET, ESR AND KINETICS OF THE OD RADICAL
00505	JCPSA-1962-36-2582	WRAY ET, KINETICS OF NO AT HIGH TEMPERATURE
00506	JCPSA-1955-23-2399	BROMBERG ET, OXIDATION OF CH4 WITH NO2
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00556	JEPOA-1971- -293	TOMANY ET, NOX CONTROL TECHNOLOGY AND DEVELOPMENT
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00708	JHTRA-1971- -365	RAMSEY ET, HEATED JET IN DEFLECTING STREAM
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00320	JIFUA-1969- -188	SNOWDON ET, H2SO4 CONDENSATION FROM FLUE GASES
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00567	JIFUA-1970- -295	SAKAI ET, COMB OF ATOMIZED FUEL OIL DROPS
00568	JIFUA-1970- -301	NURUZZAMAN ET, COMB OF MONOSIZED DROP STREAMS
00571	JIFUA-1970- -517	GIBSON, COMB OF SOLID PART IN STREAM WITH RECIRCU
00572	JIFUA-1970- -397	ARCHER ET, MULTISTAGE COMBUSTION PART 1
00573	JIFUA-1971- -196	SPALDING, COMBUSTION AS APPLIED TO ENGINEERING
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00620	JIFUA-1956-29-372	RENDLE ET,
00621	JIFUA-1967-40-342	CROSSLEY
00633	JIFUA-1953-26-122	FLINT, METAL ADDITIVES
00634	JIFUA-1969-42-67	LEE ET,
00710	JIFUA-1961- -494	THRING, TURBULENT DIFFUSION COMBUSTION, SURVEY IJ
00711	JIFUA-1970- -517	GIBSON ET, MODEL OF COMBUSTION OF SOLID PARTICLES
0071.	JIFUA-1970- -301	NURUZZAMAN ET, FLAMES ON MONOSIZED DROPLET STREAMS
00717	JIFUA-1968- -195	HAKLUYTT ET, DESIGN OF AIR REGISTERS FOR OIL-FIRED
00726	JIFUA-1971- -599	GODRIDGE ET, CARBON FORMATION IN LARGE BURNERS
00415	JOCRA-1969-45-256	BARTLE ET, TOBACCO SMOKE BY GAS CHROMATOGRAPHY
00323	JPCHA-1968-72	WHEELER, RADICAL RECOMBINATION IN SO2 DOPED FLAMES
00333	JPCHA-1965-10-	FENIMORE ET, S IN THE BURNT GAS OF H2-O2 FLAMES
00380	JPCAA-1971-21-713	STOCKHAM, COMPOSITION OF GLASS FURNACE EMISSSIONS
00381	JPCAA-1971-21-702	BAGWELL ET, BOILER OPERATING MODE FOR RED NOX
00397	JPCHA-1962-66-366	MOBERLY, SHOCK TUBE FOR HYDRAZINE DECOMPOSITION
00403	JPCHA-1966-70-1793	GUTMAN ET, THERMAL DECOMP OF N2O
00424	JPCHA-1968-72-3305	SAFRANY ET, REACTION OF H AND N WITH C2N2 HCN AND
00428	JPCHA-1969-73-2555	ASMUS ET, PYROLYSIS KINETICS OF ACETONITRILE
00520	JPCHA-1959-63-1834	FENIMORE ET, CONSUMPTION OF O2 IN HC FLAMES
00541	JPCAA-1971-21-702	BAGWELL ET, BOILER OPERATING MODES FOR REDUCED NOX
00546	JPCAA-1970-20-377	HARDISON, CONTROLLING OXIDES OF NITROGEN
00719	JPCAA-1971- -52	SCHLUCHMANN ET, N COMPUNDS OTHER THAN NO IN AUTO E
00723	JPCHA-1965-69-2111	MODICA, KINETICS OF N2O DECOMPOSITION BY MASS SPEC
00763	JPCHA-1961-65-298	FENIMORE ET, OXIDATION OF AMMONIA IN FLAMES
00321	KINFA-1969	ANON, REACTIONS OF SO,SO2, SO3 WITH H,O,OH,NO,NO2
00630	MEENA-1960-82-93	AUSTEN ET,
00631	MEENA -1960-82-92	COYKENDALL,
00404	MOPHA-1966-11-403	GOGGENHEIM, DIMERIZATION OF NO, CORRECTION
00408	MOPHA-1965-10-401	GUGGENHEIM, DIMERIZATION OF GASEOUS NO
00750	MTURA-1968-20-567	MAZUR ET, INFLUENCE OF TEMP ON COKING
00596	NACRA-1954-1158	DUGGER ET, PREDICTION OF FLAME VELOCITIES
00579	NAFTA-1970- -11.1	CHERADAME, THE AERODYNAMICS OF FLAMES
00602	NASCA-1970-TND7024	BROKAW ET, CO OXIDATION IN AUTO EXHAUST
00337	NATUA-1966- -1171	SHAW ET, OXID OF SO2 IN AIR EFFECT OF CO AND NO
00426	NATUA-1964-204-988	HERZBERG ET, IDENT OF FREE RAD IN FLASH PHOTOL
00427	NATUA-1964-203-619	MCGRATH ET, UV ABS SPECTRUM OF FREE FULMINATE
00536	NATUA-1960-186-551	SIMONS, VIBRATIONALLY HOT MOLECULES IN RADICAL REA
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00371	OIGJA-1971-9-94	BROOKS ET, CRACKING GAS OILS
00628	OIGTA-1966-NOV-66	MUNROE,
00327	PAPWA-1968-30-786	TERRY ET, OD2 BOILER AT SCUYLKULL STATION
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00336	PICMA-1963- 216	DEMARDAUCHE ET, REACTION OF S CMPDS IN FLAMES
00538	PLSSA-1967-15-643	SCHOFIELD, KINETIC RATE DATA OF ATM INTEREST
00332	PPTIA-1969-49-615	TUCKER, SOX STACK EMISSIONS-REACTIONS AND CONTROL
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00342	PRLAA-1966-295-72	CULLIS ET, HOMOGENEOUS GAS OXIDATION OF SO2
00355	PRLAA-1963-272-147,	BASCO ET, CYANOGEN RADICALS BY FLASH PHOTOL
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Table AII-3 (Cont). Literature References Alphabetized by CODEN

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00379	PRLAA-1965-288-275	SETSER ET, REACTION OF O WITH C2N2
00387	PRLAA-1963-273-145	HUSAIN ET, OXIDATION OF NH3 AND N2H4
00407	PRLAA-1968-305-93	BODEN ET, EXCITATION OF CN IN ACTIVE NITROGEN
00419	PRLAA-1970-314-585	HOMER ET, DISSOCIATION OF H2O IN SHOCK WAVES
00503	PRLAA-1956-235-89	BULEWICZ ET, HYDROGEN ATOMS IN BURNT GAS MIXTURES
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00593	PRLAA-1957-240-83	SPALDING, FLAMM LIMITS AND FLAME QUENCHING
00597	PRLAA-1970-317-227	DIXON-LEWIS ET, EXPT FUEL RICH H2 O2 N2 FLAME
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00601	PRLAA-1968-307-111	DIXON-LEWIS, TRANSPORT PHEN IN FLAMES
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00509	PYDYA-1966-4-119	CHINITZ ET, NON EQUIL HYDROCARBON AIR COMBUSTION
00540	PYDYA-1967-5-74	BAHN ET, REACTIONS INVOLVING N AND O
00729	PYDYA-1967-5-375	BAHN, CHEMICAL KINETICS N O AND H
00730	PYDYA-1968-6-101	BAHN, CHEMICAL KINETICS H+CO2=OH+CO AND
00731	PYDYA-1968-6-187	BAHN, CHEMICAL KINETICS CO2 CO HCO
00732	PYDYA-1968-6-355	BAHN, CHEMICAL KINETICS CO AND HCO
00733	PYDYA-1964-1-147	BAHN, CHEMICAL KINETICS N2 O2 NO N AND O
00734	PYDYA-1965-3-245	BAHN, CHEMICAL KINETICS H2O HO2 H2O2 O3
00735	PYDYA-1965-2-315	BAHN, CHEMICAL KINETICS H2O HO2 O3 WITH
00736	PYDYA-1965-2-197	BAHN, CHEMICAL KINETICS H2 O2 OH H AND O
00737	PYDYA-1965-2-91	BAHN, CHEMICAL KINETICS NO3 N2O NO2 O3 O2 NO N
00738	PYDYA-1967-5-221	BAHN, CHEMICAL KINETICS REACTIONS OF O AND H
00739	PYDYA-1966-4-211	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
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00743	PYDYA-1966-4-371	BAHN, CHEMICAL KINETICS F CL H O N SYSTEM
00744	PYDYA-1966-4-305	BAHN, CHEMICAL KINETICS N2H4 N2H3 N2H2
00746	PYDYA,1964-1-271	BAHN, CHEMICAL KINETICS N2O NO2 O3
00747	PYDYA-1964-1-335	BAHN, CHEMICAL KINETICS N2O NO2 O3
00751	PYDYA-1966-3-235	HILL ET, MONOETHYLAMINE COMBUSTION
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00806	REPORT	JOHNSON , GAS PHASE KINETICS OF NEUTRAL O SPECIES
00405	RIFPA-1964-19-523	JANIN ET, LA FLAMME CH4-NH3-O2
00539	SAUPA-1969-690518	TRUMPY ET, PREKNOCK KINETICS IN AN SI ENGINE
00550	SAUPA-1970-700470	CARR ET, INFLUENCE OF FUEL COMPOSITION ON CO AND
00560	SAUPA-1970-700708	CORNELIUS ET, FORMATION AND CONTROL OF NOX
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00563	SAUPA-1969-690018	NICHOLLS ET, WATER INJECTION FOR CONTROL OF NOX
00564	SAUPA-1971-710011	HEYWOOD ET, PREDICTION OF NOX IN SI ENGINE EMISSI
00402	SCIEA-1971-171-1013	WESTBERG ET, CO ROLE IN PHOTCHEMICAL SMOG
00422	SCIEA-1971-171-1013	WESTBERG ET, CO, ROLE IN PHOTOCHEMICAL SMOG
00432	SCIEA-1971-174-1341	ARCHER ET, ENVIRONMENTAL NITROSO CMPDS
00583	SCPOA-1970-58-161	COTTON, THE STRUCTURE OF FLAMES
00343	SYMCA- -12-323	MULCAHY ET, KINETICS OF O WITH SOX
00382	SYMCA-1960-8-127	FENIMORE ET, RATE OF REACTION O+N2O=NO+NO
00383	SYMCA-1965-10-435	GRAY ET, H-ATOM ABSTRATION FROM N-H BONDS
00384	SYMCA-1965-10-377	ASHMORE, REVIEW ELEMENTARY COMB REACTIONS
00418	SYMCA-1965-10-473	WESTENBERG ET, H AND O ATOM PROFILES BY ESR
00421	SYMCA-1965-10-311	CLYNE, REACTIONS OF THE HNO MOLECULE
00423	SYMCA-1960-8-487	HICKS, DECOMP FLAME OF ETHYL NITRATE
00425	SYMCA-1960-8-496	GRAY ET, FLAME OF METHYL NITRITE
00519	SYMCA-1965-10-43	WESTENBERG ET, H AND O ATOM PROFILES BY ESR IN C2
00535	SYMCA-1969-12-603	NEWHALL, ENGINE GENERATED NOX AND CO
00584	SYMCA-1953-4-267	FRISTROM ET, T PROFILES IN PROPANE-AIR FLAMES
00585	SYMCA-1971-13-997	TSUJI ET, COUNTERFLOW DIFFUSION FLAMES
00586	SYMCA-1967-11 -1057	GRAY ET, PRESENT POSITION IN EXPLOSION THEORY
00588	SYMCA-1956-6-20	LINNETT ET, LIMITS OF INFLAMMABILITY
00594	SYMCA-1958-7-475	DIXON-LEWIS ET, LIMITS OF INFLAMMABILITY
00616	SYMCA-1969-12-635	NETTLETON ET, FORMATION AND DECOMP OF SO3
00617	SYMCA-1971-13-427	MERRYMAN ET, SO3 FLAME CHEMISTRY- H2S/COS FLAMES
00623	SYMCA-1972	WENDT ET, REDUCTION OF SO3 AND NOX BY SEC FUEL
00636	SYMCA-1965-10-463	WEBSTER ET,
00637	SYMCA-1965-10-473	THRUSH ET,
00709	SYMCA-1963-9-7	BECKER ET, MIXING AND FLOW DUCTED TURBULENT JETS
00713	SYMCA-1952-4-789	THRING ET, LENGTH OF ENCLOSED TURBULENT FLAMES
00720	SYMCA-1969-12-604	NEWHALL, KINETICS OF ENGINE GENERATED NOX AND CO
00721	SYMCA-1971-13-373	FENIMORE, FORMATION OF NO IN PREMIXED HC FLAMES
00765	SYMCA-1967-11-871	MACLEAN ET, AMMONIA AND HYDRAZINE DECOMPOSITION F
00778	SYMCA	MYERSON ET, IGNITION LINITS PROPANE-NO2 FLAMES
00787	SYMCA-1963-9-560	FRISTROM,RADICAL CONC AND REACT IN CH4 O2 FLAME
00801	SYMCA-1971-13-	BREEN ET, NOX CONTROL UTILITY POWER
00805	SYMCA-1956-6-198	LEVY, DISCUSSION
00611	TASMA-1958-80-225	MARLOW,
00613	TASMA-1958-80-1231	ANDERSON ET,
00714	TASMA-1957-79-1727	SHERMAN, HEAT TRANSFER BY RADIATION FROM FLAMES
00334	TFSOA-1967-63-2442	KALLEND SO2 ON CHEMILUM AND ATOM RECOMBINATION
00345	TFSOA-1946-42-354	DOOLEY ET, OXIDATION OF SO2 IN GAS FLAMES
00352	TFSOA-1953-49-1312	MADLEY ET, KINETICS OF OXID OF CHARCOAL WITH N2O
00385	TFSOA-1968-64-1836	DAVIES ET, REACTION OF O WITH HCN, CNCL AND CNBR
00409	TFSOA-1967-63-1687	CERCEK ET, REACTION OF H AND OH WITH PYRIDINE
00501	TFSOA-1956-52-1475	BULEWICZ ET, DISSOCIATION CONSTS BY FLAME PHOTOMET
00502	TFSOA-1956-52-1465	SUGDEN, DISSOCIATION CONSTS BY FLAME PHOTOMETRY I
00513	TFSOA-1967-63-662	GILES ET, REACTIONS OF RF3 RADICALS WITH ORGANIC H
00523	TFSOA-1957-53-1102	HOARE ET, REACTION OF CH3 WITH O2 AND COMPARISON
00635	TFSOA-1966-62-2150	JOFFE ET,
00639	TFSOA-1969-65-3013,	HALSTEAD ET,
00762	TFSOA-1968-64-71	BRADLEY ET, OXIDATION OF NH3 IN SHOCK WAVES
00716	THENA-1968-15-44	IVANOV, FLOW SECTION OF VORTEX BURNERS
00788	THESIS-1967	MORGAN, COMB OF CH4 IN A JET STIRRED REACTOR
00725	TORFA-1963-40-28	RAKOVSKII ET, PYROLYSIS OF PYRIDINE AND QUINOLINE
00372	TOSCA- -6-106	LINNELL, THERMAL DECOMPOSITION OF PYRIDINE
00706	VGBGA-1969-1133	NIEPENBERG, DESIGN FEATURES OF GAS BURNERS
00344	ZFKHA-1940-14-1428	ANON, GENERAL PHYSICAL CHEM
00527	ZFKHA-1959-33-572	NIKITIN, THERMAL DISSOCIATION OF DIATOMIC MOLECULE
00627	ZFKHA-1940-14-1428	BOREKOV ET, KINETICS OF REACTION OF NO2 AND SO2

Table AII-4

CODEN NAMES FOR JOURNALS, ALPH BY NAME OF JOURN

APMPA	AIR POLLUTION CONTROL ASSN, PAPER
AICEA	AM INST OF CHEM ENGINEERS, JOURNAL
ARPLA	ANN REVIEW OF PHYSICAL CHEMISTRY
AICPA	AM INST OF CHEM ENG, PAPAER
AAPRA	AM INST OF AERONAUTICAL AND ASTRONAUT ENG, PAPER
AIAJA	AM INST OF AERONAUT ANS ASTRONAUT ENG, JOURNAL
ACPYA	ACTA PHYSICOCHIM URSS
AGPTA	AMERICAN GAS ASSN PAPER
PAPGA	AMERICAN PETROLEUM INST PROCEEDINGS SECTION 1
ACIEA	ANGEWANDETE CHEMIE (INT ED)
ASMSA	ASME PREPRINT
AJCHA	AUSTRALIAN JOURNAL OF CHEMISTRY
PPTIA	AMERICAN PETROLEUM INSTITUTE, PROCEEDINGS
BRWKA	BRENNST-WARME-KRAFT
BCHEA	BRITISH CHEMICAL ENGINEERING
BCSJA	BULL CHEM SOC JAPAN
BSCBA	BUL SOCIETE CHIE BELGES
BBCUA	BRITISH COAL UTILIZATION RES ASSN, BULLETIN
CHBEA	CHEMISCHE BERICHTE
CEPRA	CHEMICAL ENGINEERING PROGRESS
CESCA	CHEMICAL ENGINEERING SCIENCE
CITEA	CHEMIE-ING-TECH
CIEAA*	COMBUSTION INSTITITE, EASTERN SECTION, PAPERS
CRADA	COMPTES RENDUS DE L/ACADEMIE DES SCIENCES, PARIS
CENEA	CHEMICAL AND ENGINEERING NEWS
CJCEA	CANADIAN JOURNAL OF CHEMICAL ENGINEERING
CPENA	CHEMICAL AND PROCESS ENFINEERING
CHREA	CHEMICAL REVIEWS
CBFMA	COMBUSTION AND FLAME
CBSTA	COMBUSTION SCIENCE AND TECHNOLOGY
WCIPA	COMBUSTION INSTITUTE, WESTERN STATES SECT, PREPRINT
WSCPA	COMBUSTION INSTITUTE, WESTERN STATES SECT, PAPER
CJCHA	CANADIAN JOURNAL OF CHEMISTRY
DKPCA	DOKLADY, PHYSICAL CHEMISTRY SECTION, ENGLISH
ELWOA	ELECTRICAL WORLD
ESTHA	ENVIRONMENTAL SCIENCE AND TECHNOLOGY
ERKOA	ERDOL UND KOHLE
FUELA	FUEL
RLBUA	GENERAL ELECTRIC RESEARCH LAB BULLETIN
HCACA	HELVETIA CHIMICA ACTA
IJCKA*	INTERNATIONAL JOURNAL OF CHEMICAL KINETICS
IEPDA	INDUSTRIAL AND ENGINEERING CHEM, PROCESS DESIGN
ICONA*	INCINERATION CONFERENCE, 1970
IECHA	INDUSTRIAL AND ENGINEERING CHEMISTRY
IENAA	IND ENG CHEM, ANALYTICAL ED
IERSA	IND ENG CHEM, ANN REV SUPP
IECFA	IND ENG CHEM, FUNDAMENTALS
IECIA	IND ENG CHEM, INDUSTRAIL ED
IEIEA	IND ENG CHEM, INTERNATIONAL ED
IEPRA	IND ENG CHEM, PRODUCT RESEARCH AND DEV
IJCEA	INTERNATIONAL JOURNAL OF CHEMICAL ENGINEERING *
INCEA	INTERNATIONAL CHEMICAL ENGINEERING
BUPAA	INSTITUTE OF PAPER CHEMISTRY, BULLETIN

Table AII-4 (Cont). CODEN Names for Journals, Alph by Name of Journ

JFLSA	JORUNAL OF FLUID MECHANICS
JPLRA	JET PROPULSION LAB TECH REPT
JPCAA	JOURNAL OF THE AIR POLLUTION CONTROL ASSN
JACSA	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
JAMCA	JOURNAL OF APPLIED MECHANICS, ASME, SERIES E
JCPSA	JOURNAL OF CHEMICAL PHYSICS
JOCRA	JOURNAL OF CHROMATOGRAPHY
JEPOA	JOURNAL OF ENGINEERING FOR POWER
JFIRA*	JOURNAL OF FIRE AND FLAME
JIFUA	JOURNAL OF THE INTITUTE OF FUEL
JPCHA	JOURNAL OF PHYSICAL CHEMISTRY
JAHSA	JOURNAL OF THE ATMOSPHERIC SCIENCES
JHTRA	JOURNAL OF HEAT TRANSFER
JNBAA	JOURNAL OF RESEARCH OF THE NATIONAL BUREAU OF STANDARDS
MECCA*	MECHANISM OF CORROSION BY FUEL IMPURITIES
MEENA	MECHANICAL ENGINEERING (ASME)
MTURA	METALURGIA, BUCHAREST
MOPHA	MOLECULAR PHYSICS
NACRA	NAT AD COMM FOR AERONAT, REPT
NAFTA*	NORTH AMERICAN FUEL TECH CONF
NATUA	NATURE
NASCA	NATIONAL AERONAUTICS ANS SPACE ADMIN, TECH NOTE
PLSSA	PLANETARY AND SPACE SCIENCE
PCSLA	PROCEEDINGS OF THE CHEMICAL SOCIETY, LONDON
PYDYA	PYRODYNAMICS
PAPWA	PROC OF THE AMERICAN POWER CONFERENCE
PTRSA	PHIL TRANS OF THE ROY SCOIETY
PAPWA	PROCEEDINGS OF THE AMERICALN POWER CONF
PRLAA	PROC OF THE ROYAL SOCIETY (LONDON) SERIES A
PICMA*	PROCEEDINGS OF THE INTERNATIONAL CONF ON THE MECH OF CORROSION
PSRIA*	PROCEEDINGS OF AN INTERN SYMP ARRANGED BY STANFORD RES INSTITUE
RADCA*	RADIATION CHEMISTRY
RIFPA	REVUE DE L'INSTITUT FRANCAISE DE PETROLE
SCPOA*	SCIENCE PROGRESS/OXFORD
SCIEA	SCIENCE
SAUPA	SOCIETY OF AUTOMOTIVE ENGINEERS PAPER
SYMCA	SYMPOSIUM ON COMBUSTION (INTL)
THENA	THERMAL ENGINEERING, USSR
TASMA	TRANSACTION S OF THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
TFSOA	TRANACTIONS OF THE FARADAY SOCIEITY
TOSCA	TOBACCO SCIENCE
OIGJA	THE OIL AND GAS JOURNAL
KINFA*	US DEPT COMM, NAT BUR STDS, KINETICS INFO CENTER
VGBGA*	VGB CONVENTION ON GAS HEATING
ZFKHA	ZHURNAL FIZ KHIM
ZPKHA	ZHURNAL PRIK KHIM

Table AII-5

CODEN NAMES FOR JOURNALS, ALPHA BY CODEN

AAPRA	AM INST OF AERONAUTICAL AND ASTRONAUT ENG, PAPER
ACIEA	ANGEWANDETE CHEMIE (INT ED)
ACPYA	ACTA PHYSICOCHIM URSS
AGPTA	AMERICAN GAS ASSN PAPER
AIAJA	AM INST OF AERONAUT ANS ASTRONAUT ENG, JOURNAL
AICEA	AM INST OF CHEM ENGINEERS, JOURNAL
AICPA	AM INST OF CHEM ENG, PAPAER
AJCHA	AUSTRALIAN JOURNAL OF CHEMISTRY
APMPA	AIR POLLUTION CONTROL ASSN, PAPER
ARPLA	ANN REVIEW OF PHYSICAL CHEMISTRY
ASMSA	ASME PREPRINT
BBCUA	BRITISH COAL UTILIZATION RES ASSN, BULLETIN
BCHEA	BRITISH CHEMICAL ENGINEERING
BCSJA	BULL CHEM SOC JAPAN
BRWKA	BRENNST-WARME-KRAFT
BSCBA	BUL SOCIETE CHIE BELGES
BUPAA	INSTITUTE OF PAPER CHEMISTRY, BULLETIN
CBFMA	COMBUSTION AND FLAME
CBSTA	COMBUSTION SCIENCE AND TECHNOLOGY
CENEA	CHEMICAL AND ENGINEERING NEWS
CEPRA	CHEMICAL ENGINEERING PROGRESS
CESCA	CHEMICAL ENGINEERING SCIENCE
CHBEA	CHEMISCHE BERICHTE
CHREA	CHEMICAL REVIEWS
CIEAA*	COMBUSTION INSTITITE, EASTERN SECTION, PAPERS
CITEA	CHEMIE-ING-TECH
CJCEA	CANADIAN JOURNAL OF CHEMICAL ENGINEERING
CJCHA	CANADIAN JOURNAL OF CHEMISTRY
CPENA	CHEMICAL AND PROCESS ENFINEERING
CRADA	COMPTES RENDUS DE L/ACADEMIE DES SCIENCES, PARIS
DKPCA	DOKLADY, PHYSICAL CHEMISTRY SECTION, ENGLISH
ELWOA	ELECTRICAL WORLD
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FUELA	FUEL
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IJCKA*	INTERNATIONAL JOURNAL OF CHEMICAL KINETICS
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JACSA	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
JAHSA	JOURNAL OF THE ATMOAPHERIC SCIENCES
JAHSA	JOURNAL OF THE ATMOSPHERIC SCIENCES
JAMCA	JOURNAL OF APPLIED MECHANICS, ASME, SERIES E
JCPSA	JOURNAL OF CHEMICAL PHYSICS

Table AII-5 (Cont). CODEN Names for Journals, Alpha by CODEN

JEPOA	JOURNAL OF ENGINEERING FOR POWER
JFIRA*	JOURNAL OF FIRE AND FLAME
JFLSA	JORUNAL OF FLUID MECHANICS
JHTRA	JOURNAL OF HEAT TRANSFER
JIFUA	JOURNAL OF THE INTITUTE OF FUEL
JNBAA	JOURNAL OF RESEARCH OF THE NATIONAL BUREAU OF STANDARDS
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MOPHA	MOLECULAR PHYSICS
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NATUA	NATURE
NASCA	NATIONAL AERONAUTICS ANS SPACE ADMIN, TECH NOTE
OIGJA	THE OIL AND GAS JOURNAL
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PCSLA	PROCEEDINGS OF THE CHEMICAL SOCIETY, LONDON
PICMA*	PROCEEDINGS OF THE INTERNATIONAL CONF ON THE MECH OF CORROSION
PLSSA	PLANETARY AND SPACE SCIENCE
PPTIA	AMERICAN PETROLEUM INSTITUTE, PROCEEDINGS
PRLAA	PROC OF THE ROYAL SOCIETY (LONDON) SERIES A
PSRIA*	PROCEEDINGS OF AN INTERN SYMP ARRANGED BY STANFORD RES INSTITUE
PTRSA	PHIL TRANS OF THE ROY SCOIETY
PYDYA	PYRODYNAMICS
RADCA*	RADIATION CHEMISTRY
RIFPA	REVUE DE L'INSTITUT FRANCAISE DE PETROLE
RLBUA	GENERAL ELECTRIC RESEARCH LAB BULLETIN
SAUPA	SOCIETY OF AUTOMOTIVE ENGINEERS PAPER
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WSCPA	COMBUSTION INSTITUTE, WESTERN STATES SECT, PAPER
ZFKHA	ZHURNAL FIZ KHIM
ZPKHA	ZHURNAL PRIK KHIM

Table AII-6

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Appendix III. Simulation of Flame Fronts by "Point-Wise" Kinetic Calculations

The flame in a premixed or diffusion flame of a highly combustible system, is very thin but of finite thickness. The thickness can be regarded as the distance over which convectional, diffusional and reaction mechanisms, are all significant so that none can be neglected. The exact solution of the governing equation for any but the simplest kinetics schemes is very formidable involving as it does an elliptic set of differential equations and (possibly) stiff kinetics. Only for very simple systems (See 789) have "exact" solutions been obtained.

In this Appendix we describe methods by which the diffusional processes can be taken into account in a rough manner so as to provide estimates of flame thickness, flame speed, and the concentrations of all species at a representative point in the flame front. While for many systems the approximations that have to be made are not valid, e.g., CDS flames where multiple flame fronts are observed (794), there are also many systems where they probably are permissible. For exploratory calculations it is not advisable to expend a great deal of effort in supposedly exact simulation of diffusional effects when the kinetic mechanism is known only very approximately.

Premixed Flat Laminar Flames

For this case we approximate the flame front by a reactor with back diffusion with the Wehner-Wilhelm boundary conditions.

At the inlet, the total flux of each component is specified.
At the outlet, the diffusive flux of each component is zero.

A sketch of the reactor is shown in Figure AIII-1, with a typical concentration gradient for one of the components. We approximate the concentration profile by the quadratics

$$y_i = a_i + b_i x + c_i x^2 \qquad \text{AIII-1}$$

Conditions are imposed to permit evaluation of the undertermined constants a_i, b_i, c_i, h_i, and N_t, the total flux.

These conditions are:

(1) Mole fraction at the outlet is y_i^e. For the "fuel" **specie the exit mole fraction is specified** (y_{fuel}^e).
(2) Gradient of mole fractions at the outlet are zero for all components.
(3) Flux of each species at the inlet section is $N_t z_i^{in}$.
(4) Mole fraction of the "fuel" species at the inlet is y_{fuel}^{in}.
(5) The "point-wise" rate of reaction at the exit section matches the material balance for each component, i.e., equation **A III-3 is satisfied at the exit** section.

The governing equations for the case where the fluxes of all components are parallel are the Maxwell Stefan equations.

$$\frac{dy_i}{dx} = -N_i \sum \frac{y_j}{\rho_m D_{ij}} + y_i \sum \frac{N_j}{\rho_m D_{ij}} \qquad \text{A III-2}$$

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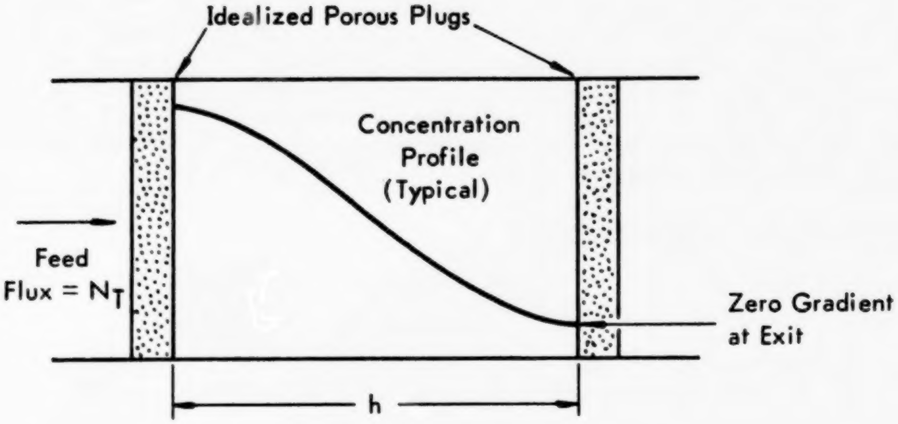
Idealized Porous Plugs
Concentration Profile (Typical)
Feed Flux = N_T
Zero Gradient at Exit
h

Figure AIII-1. CONCEPTUAL SKETCH OF FLAME FRONT IN A LAMINAR PREMIXED FLAME and the material balance for the species i is

$$\frac{dN_i}{dx} = R_i \qquad \text{A III-3}$$

In these approximate calculations we assume that the product of density and binary molar diffusivities for all components and for all x can be replaced by a single average value. We also neglect the change in the total number of moles flowing past any section. With these approximations the governing equations become:

$$\rho_m D \frac{dy_i}{dx} = -N_i + y_i N_t \qquad \text{A III-4}$$

$$N_i = -\rho_m D \frac{dy_i}{dx} + y_i N_t \qquad \text{A III-5}$$

$$\frac{dN_i}{dx} = \rho_m D \frac{d^2 y_i}{dx^2} + N_t \frac{dy_i}{dx} = R_i \qquad \text{A III-6}$$

Using the equations and the boundary conditions we find after some manipulation:

$$\left(\frac{h}{N_t} + \frac{h^2}{2\rho_m D}\right) R_i^e + y_i^e = z_i^{in} \qquad \text{A III-7}$$

This may be compared with the governing equations for a perfectly stirred reactor.

$$(\mathrm{VOL})\, R_i = y_i^e - z_i^{in} \qquad \text{A III-8}$$

Hence the "point-wise" material balance is the same as for a perfectly stirred reactor with reciprocal space velocity VOL where

$$\mathrm{VOL} = \frac{h}{N_t} + \frac{h^2}{2\rho_m D} \qquad \text{A III-9}$$

And now using the imposed conditions, the length of the reactor h and the throughput N_t, which lead to the specified inlet and exit concentrations for the "fuel" species are found to be

$$h = \sqrt{2(1-\zeta)} \quad \sqrt{\rho_m D(\mathrm{VOL})} \qquad \text{A III-10}$$

$$N_t = \sqrt{\frac{2(1-\zeta)}{\zeta^2}} \quad \sqrt{\frac{\rho_m D}{\mathrm{VOL}}} \qquad \text{A III-11}$$

where

$$\zeta = \left[\frac{1 - y_{fuel}^{in} / z_{fuel}^{in}}{1 - z_{fuel}^{e} / z_{fuel}^{in}}\right] \qquad \text{A III-12}$$

At this stage the concentrations y^{in}_{fuel} and z^{e}_{fuel} of the fuel at the inlet and exit of the reactor are arbitrary. We must select values which can be expected to give a fair representation of the conditions at the flame front. The exit section, for a good simulation, ought to coincide approximately with the section where the rate of consumption of fuel is a maximum, and the inlet section should be placed where the reaction is very slow and yet the quadratic approximation to the concentration profiles is not seriously in error. Tentatively we take the make the following assignments.

$$z^{e}_{fuel} = 0.1\ z^{in}_{fuel} \qquad \text{A III-13}$$

$$y^{in}_{fuel} = 0.5\ z^{in}_{fuel} \qquad \text{A III-14}$$

Therefore the "equivalent" Wehner-Wilhelm reactor encompasses the region from the midpoint of the flame front to the point where the conversion of the fuel is ninety percent. The validity of these assignments can only be justified by comparison of the predicted results with data.

Inserting these values for y^{in}_{fuel} and z^{e}_{fuel} into equations A III-10 and A III-11 we find:

$$h = 0.94\sqrt{\rho_m D\ (VOL)} \qquad \text{A III-15}$$

$$N_t = 1.7\sqrt{\rho_m D\ (VOL)} \qquad \text{A III-16}$$

To calculate N_t and h we need to select an appropriate average diffusion coefficient. In the expectation that diffusion of heat is more important that than diffusion of active species we suggest taking $\rho_m D$ to be equal to k/C_{pm} evaluated at the exit temperature and composition in the Wehner-Wilhelm reactor.

Diffusion Flames Modeled by the Whitman Two-Film Theory

In real diffusion flames, the physical conditions near the flame front are influenced in a very complex way by the turbulence in the system. We cannot hope to model these processes very exactly. Instead we adopt the conventional chemical engineering approach of using equivalent film thicknesses in the Whitman two film model with film thicknesses the same as for the case where chemical reactions do not occur. This theory then can be regarded as a means for correcting for the effects of the chemical reactions.

We consider the steady state system sketched in Figure A III-2. On the right is fuel gas with a composition specified at the boundary, X=c. Similarly, on the left is the oxidizer gas with composition specified at x=0.Between these two sections the concentration varies because of diffusion alone in zones A and B and because of combined diffusion and reaction in zone R.

As in the case of the premixed flame model we take the diffusion coefficients D_{ij}, for all species to be the same and to be independent of position. We also assume that there is no net generation of moles at the reaction front.

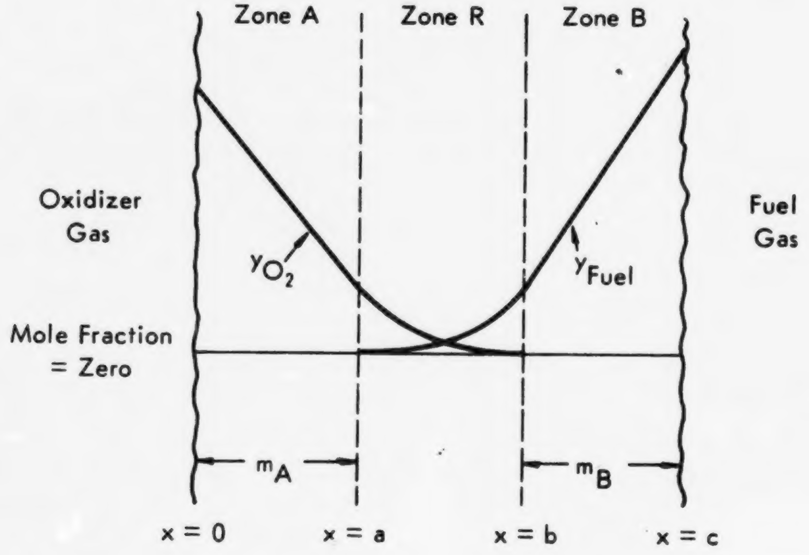
Zone A
Zone R
Zone B
Oxidizer Gas
Fuel Gas
y_{O_2}
y_{Fuel}
Mole Fraction = Zero
m_A
m_B
x = 0
x = a
x = b
x = c

Figure AIII-2. CONCEPTUAL SKETCH FOR DIFFUSION FLAME FRONT

With these approximations the governing equations are

$$\rho_m D \frac{dy_i}{dx} = -Ni \qquad \text{A III-17}$$

$$\frac{dN_i}{dx} = R_i \qquad \text{A III-18}$$

and the solutions for the zones where reaction can be neglected are

$$N_i = \rho_m D \ (y_i - y_i) / m \qquad \text{A III-19}$$

In zone R, reactions can not be neglected. We take them into account by a"point-wise" calculation. In the reaction zone the concentration profiles for all species are assumed to follow the quadratic equations

$$y_i = A_i + B_i x + C_i x^2 \qquad \text{A III-20}$$

Boundary conditions are imposed on these equations at both edges of zone R to match the concentrations and slope on the side where the reactant is being supplied and to make the value and slope of that species zero at the opposite boundary. The fluxes entering the reaction zone must also be specified. Appealing to the Burke-Schumann model of the diffusion flame we take the fuel and oxidizer fluxes to be equal to that corresponding to stoichiometric combustion to a specified set of products. For example when burning methane we may assume that the products are CO and H_2O rather than CO_2 since the rate of reaction to the CO stage is much faster than that to the CO_2 stage. The assumption of arbitrary products can not be removed from the model at this stage of sophistication. To do this would require a more elaborate model. We also assume that the reaction zone R is very thin compared to zones A and B.

With these approximations we find for the oxidizer (for example) the following relations:

$$R_{ox} = \frac{-\rho_m D(y_{ox}^{feed} - y_{ox}^{prod})y_{ox}^{feed}}{8m_A^2 y_{ox}^{prod}}$$

Comparing this with the governing equations for a perfectly stirred reactor, we see that we can identify the rate at which reactants diffuse up to the reaction front (combustion intensity) with the following function of the equivalent reciprocal space velocity:

$$N_{ox} = \sqrt{\frac{8\rho_m D y_{ox}^{feed} y_{ox}^{prod}}{(VOL)}}$$

Appendix IV. Description of Computer Program EXHAUS for Integrating Stiff Differential Equations Arising in Kinetics Problems

Abstract

A computer program, EXHAUS, for integrating sets of differential equations arising from kinetics problems is described. This program, which uses "a cantilevered implicit method" is especially suitable for systems of "stiff" equations such as result from problems with great disparity in characteristic reaction times, for example, combustion problems. Use of free format and internal tables of thermochemical and rate constant data make the program especially easy to use. Either well-mixed stages or plug flow reactors or combinations of these types can be simulated with specified temperature histories or under heat balanced conditions. The integration method, TYSON, can be used independently of the chemical reaction features for difficult-to-integrate problems.

Purpose and Scope

Program EXHAUS integrates the conservation equations for individual chemical species for a stirred-tank or plug-flow reactor. Temperature and pressure may be specified as functions of residence time in the reactor or a heat-balanced solution may be obtained. Up to 35 species may be handled. The reactions (up to 70 in number) may be unimolecular, bimolecular or termolecular provided they can be represented by

$$A + B + C \rightleftharpoons D + E + F$$

where A, B, C, D, E, F represents a molecule or molecular fragment. One of two of the reactants or products can be missing. If a species is mentioned on both sides of the $\rightleftharpoons$ sign it is taken to represent a non-reacting third body. The species name "M" represents a generalized third body. The program treats all species as ideal gases; however, liquid phase reactions can be simulated by use of a (large) effective pressure.

The method of integration used is based on the paper "An Implicit Integration Method for Chemical Kinetics" by T. J. Tyson (795). It is also discussed in reference (796). This method of integration, which we call a "cantilevered inplicit method" is especially suited to the integration of "stiff" equations such as arise when some of the species react very much faster than some other species as, for example, in combustion. No special precautions need be taken when formulating the equations to eliminate nearly equilibrated reactions as must be done, for example, when using explicit (predictor-corrector or Runge Kutta) methods. For reaction systems which are not "stiff" the program described is somewhat slower than explicit methods but it will often be found useful because of its convenient input and its general reliability. Since it is an implicit method, the program must calculate the partial derivatives of the rate expressions with respect to temperatures and the concentrations. This is done "analytically" under the assumption that the reactions are of integral order as implied by the way in which they are written and that the reaction rates can be calculated from

$$r_f = a_f \; Z_f \; T^{nf} \exp\left[-E_f/rt\right] \; C_a \; C_b \; C_c$$
$$r_r = a_r \; Z_r \; T^{nr} \exp\left[-E_r/AT\right] \; C_d \; C_e \; C_f$$

If less than three reactants or products are involved, the corresponding concentration in these equations are replaced by unity.

Output Generated

After printing out the input data the program calcuates, prints and plots (on the line printer) the temperature, pressure, gas density and species mole fractions as a function of residence time. A time step of variable size is used in the integration to reduce calculation time. The program also prints out the forward and reverse rates for each of the reactions considered at a number of time steps. This permits one to readily assess the importance of particular reactions and to determine which reactions are at equilibrium.

Sample Problem

Appendix V shows input and output for one of the simulations described in this report.

Problem Setup

The user will go through five phases in setting up a problem to be run on EXHAUS. First he must specify the type and size of reactor, whether plug flow, series of well mixed stages, or a series of well mixed stages followed by a plug flow reactor. Second, he must specify the kinetic mechanism, components and reactions with their rate constants. Third, he must specify amount and type of output. Fourth, he may wish to alter the normal accuracy criterion and other integration control parameters. The last phase is program execution.

This program uses a "free-format with control word" type of data card. Columns 1-6 of each card contain a control word (for example: VOLUME, EXECUT....) which functions as a machine instruction, directing the setting of a set of data or the use of a particular option. Card order in the data deck is immaterial (with certain minor and obvious exceptions e.g. the EXECUT card is the last in each data deck). Below we describe briefly the function of each type of data card under the five phases of data preparation. Precise statements of the format of each type of card are given in **Tables AIV-1 and AIV-2**.

Phase I Reactor Configuration and Size

NUMWSS	Sets number of well stirred stages, may be zero.
PLUGFLOW	Calls for a plug flow reactor following the (NUMWSS)well stirred stages.
FLAME or IGNITE	Selects method used to calculate the well stirred stages. We recommend FLAME.
VOLUME	Determines the reciprocal space velocity of the well stirred stages.
TIMEIN and TIMOUT	Sets the range of the independent variable (time or reciprocal space velocity) for the plug flow reactor.

HTLOSS	Determines the factors governing heat loss.
HEATBALANCE	Selects a heat balanced case as contrasted with specified temperature and pressure.
PDECAY	Sets the pressure or pressure-time profile.
TDECAY	Sets the temperature-time profile.

Phase II Defines the reacting system in terms of species and reactions.

SPECIE	Defines a chemical species and sets its mole fraction in the feed and estimate of mole fraction in product.
HSFORM	Feeds in heat of formation, entropy of formation and other molecular properties.
CPCONS	Feeds in specific heat data.
STOICH	Defines an elementary chemical reaction.
FRATCO	Feeds in Arrhenius rate parameters for the forward direction of a reaction.
RRATCO	Feeds in Arrhenius rate parameters for the reverse direction of a reaction.

For certain species and reactions the HSFORM, CPCONS, FRATCO and RRATCO cards are not needed. Internally stored data will be used.

Phase III Output Control

PRINTP	Determines the maximum change in independent variable tolerated without output.
NRITE	Determines the frequency of detailed output. Suggested value 10.
DEBUG1 DEBUG2 BUGPRI	Determine degree of debug printout called for. For normal printout omit these cards.

Phase IV Integration Control

If not placed in the data deck, standard values for these parameters will be used.

SSCONT	Sets a parameter controlling step size.
STEPIN	Gives an initial step size. If a value greater than 1000.0 is given the program calculates step size automatically
MAXTRY	Gives the maximum allowed number of trials in program IGNITE.

Phase V The Execute Card

EXECUT	Turns control over to the machine to solve the problem and prints out the answer.

Table AIV-1

FORMAT OF CONTROL AND DATA CARDS

Program EXHAUS

(1) To acquire and execute program

```
- your run card -
@ XQT CUR
  FSTIN  COMBF4/409560
@N XQT EXHIGN
```

data deck for your
problem
ends with an EXECUTE card

stacked data deck for
second case - with selected
variables reset
ends with an EXECUTE card

```
@N XQT  EXHIGN
```

stacked data deck with
all variables reset
ends with an EXECUTE card

(2) General comments on data cards

(a) Columns 1-6 are ordinarily for an identifier word [illegible], BUGPRI, SSCONT, STEPIN, TIMEIN, TIMOUT, PRINTD, TDECAY, FDECAY, FRATCO, RRATCO, STOICH, SPECIE, CONSTR, DEBUG1, DEBUG2, NUMWSS, HSFORM, CPCONS, FLAME, PLUGFL, HEATBA, MAXTRY, NRITE or EXECUT.

(b) The card is punched free format with fields delimited by commas (or in the case of STOICH cards by + and = also). Blanks are not significant. Decimal points need not be punched. Large (or small numbers) may be represented by a magnitude multiplied by a power of 10. e.g. 123.4E-7.

(c) Card order is not significant except for the following points.
  (c1) The FRATCO and RRATCO cards must follow the STOICH cards for the corresponding reaction.
  (c2) The HSFORM and CPCONS cards must follow the (SPECIE or STOICH) card which first introduces the corresponding species.
  (c3) The EXECUT card must be the last in the deck for that run.

(d) Certain "default" variables are built into the program. If the user does not insert a card to set these the following cards are "understood" to be present:

Table AIV-1 (Cont). Format of Control and Data Cards

```
PDECAY, 1.0, 1.0, 0.0
STEPIN, 1000.0
SSCONT, 0.05
TIMEIN, 0.0
DEBUG1, 1
DEBUG2, 1000
MAXTRY, 200
NUMWSS, 1
```

(e) The program has built-in libraries of thermochemical constants and Arrhenius rate parameters. Data cards CPCONS and HSFORM have precedence over the internally stored data and likewise FRATCO and RRATCO take precedence over the internally stored rates.

(f) Species names are left adjusted using the first 6 characters only and filling in on the right with blanks if there are fewer than 6 characters.

(g) Reactions are written with , + and = signs to delimit fields; the = sign separates the reactants from the products. By convention M represents a general gaseous third body.

Table AIV-2. FORMAT OF DATA CARDS

(Identifier Word in First Field	Successive fields are separated by commas, e.g. ,< >, < >,
******	< title of problem >
TIMEIN,	< starting time, sec or starting volume, cm^3 >
TIMOUT,	< final time, sec, or final volume, cm^3
TDECAY,	< feed temperature, °K >, < temp, °Kat instant of starting >, < time interval, TIMP sec >, < not used >. <guess, °K, at temperature of adiabatic well stirred stage>
PDECAY,	< system pressure, atm, or, for liquid systems the effective pressure >
BUGPRI,	<< use this card if debug printout is required, otherwise omit >>
SSCONT,	< the step size control parameter, usually 0.05; >
STEPIN,	< the starting step size, sec or cm^3 >
PRINTD,	< minimum printout interval, sec >
SPECIE,	< name of a species >, < mole fraction in feed>, < guess as to mole fraction in product of stirred reactor >
STOICH,	< a 6 character identifier >,< reaction written symbollically, e.g. A+B+C=D+E+F >
FRATCO,	< a 6 character identifier >,< a_f >, < Q_f >, <n_f >, < E_f >
PRATCO,	< a six-character identifier >, < a_r >, < Q_r >, < n_r >, < E_r >
CPCONS,	< name of a species >, < ACP >, < BCP >, < CCP > , < DCP >
HSFORM,	< name of a species >, < ΔH_f >, < S_f >
VOLUME,	< volume of well stirred reactor, cm^3 /(g mole / sec) >
DEBUG1,	< number of consecutive steps to be printing with debug printout >
DEBUG2,	< number of consecutive steps to be skipped before debug printout >
NUMWSS,	< number of well stirred reactors in series >
FLAME ,	<< insert this card to force use of program FLAME >
PLUGFL,	<< insert this card to force calculation of a plut flow reactor following the stirred tank reactor >>
HEATBA,	<< insert this card to force a heat balance, or omit for specified temp or pressure >>
MAXTRY,	< maximum number of trials allowed in solving stirred tank reactor >
EXECUT,	Causes program to execute the case described by the above cards.
NRITE ,	< number of steps between successive detailed printouts, recommend 10 >
IGNITE,	<< insert this card if method IGNITE is to be used for well stirred stage calculation>>
FUEL ,	< species number of species identified as fuel >
OXIDIZ,	< species number of species identified as oxidizer >
DILUEN,	< species number of species identified as diluent >
HTLOSS,	< ambient temperature °K >, < radiative heat loss coefficient, cal/sec cm^3(°K^4>, < convective heat loss coefficient, cal/sec, cm ^{3} (°K) >

Appendix V. An Exhibit of the Computer Output Generated by Program EXHAUS

In order to show how EXHAUS is used and what types of output information are generated, we give here a copy of the entire output for a typical modelling problem. The problem displayed is that described in the section entitled "NO Reduction by Secondary Fuel Injection (Reburning)." The problem name is WILD 6. Because of its size, the complete listing is not included herein, but is available through the U.S. Environmental Protection Agency.